

ACYCLIC DIENE METATHESIS (ADMET)
POLYMERIZATION:
A HYDROCARBON STRUCTURE REACTIVITY STUDY

By

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"The reasonable man adapts himself to the world: the unreasonable one persists in trying to adapt the world to himself. Therefore all progress depends on the unreasonable man."

George Bernard Shaw

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Abstract of Dissertation Presented to the Graduate School
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ACYCLIC DIENE METATHESIS (ADMET)
POLYMERIZATION: A HYDROCARBON STRUCTURE
REACTIVITY STUDY

By
James Konzelman

May 1993

Chairman: Professor Kenneth B. Wagener
Major Department: Chemistry

The relationship between the structure and reactivity of hydrocarbon olefins was investigated for the acyclic diene metathesis (ADMET) polymerization reaction. This new step condensation polymerization requires the use of highly active Lewis acid free metathesis catalysts of the type, $M=CHR(N-2,6-C_6H_3-i-Pr_2)[OCMe(CF_3)_2]_2$ ($M = W$ or Mo). The tungsten and molybdenum based catalysts employed in this study demonstrated marked differences in catalytic ability, with the molybdenum catalyst proving more versatile.

The first copolymers synthesized via ADMET techniques are reported. 1,9-Decadiene and 1,5-hexadiene were copolymerized in a series of varying monomer feed ratios. The microstructure of the copolymers has been defined by statistical analysis of the dyad

sequences observed by quantitative ^{13}C NMR. As predicted by the step nature of the ADMET mechanism, these copolymers possess a random sequence distribution.

Model compound studies of 1,1-disubstituted and tri-substituted olefins defined the structure for potential ADMET monomers. The tungsten catalyst proved to be ineffective in the catalysis of these compounds, while the molybdenum based catalyst successfully polymerized 2-methyl-1,5-hexadiene to 1,4-polyisoprene. The selectivity of the tungsten based catalyst was exploited for the synthesis of a series of alternating copolymers from trienes that contained only two reactive olefin groups.

Both the tungsten and the molybdenum based catalysts were successful in the metathesis of alpha substituted olefins; however, the tungsten catalyst was incapable of producing the quantitative yields demonstrated by the molybdenum catalyst. Consequently, the molybdenum catalyst was employed in the ADMET polymerization of 3-methyl-1,5-hexadiene, *cis*-1,2-divinylcyclohexane and *trans*-1,4-divinylcyclohexane. Additionally, the stereoselectivity of the metathesis of alpha substituted olefins was examined, as a preference for the *cis* stereoisomer was observed.

CHAPTER 1

INTRODUCTION

The literal meaning of the word metathesis is the transposition of letters, syllables, or sounds in a word,¹ but when applied to chemistry, metathesis takes on new meaning:

Metathesis- *Chem.* a reaction whose result is the interchange of two parts of two substances to form two new substances, as



also called double disproportionation.¹

More specifically, the term 'olefin metathesis', first applied by Calderon in 1967, describes the interchange of carbon atoms between a pair of carbon-carbon double bonds (Figure 1-1).²

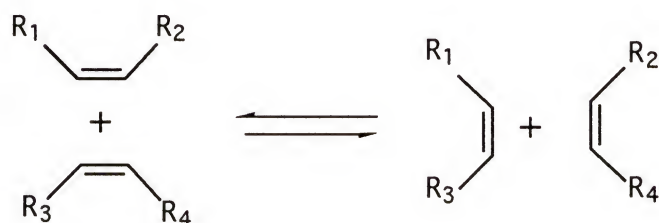


Figure 1-1. General olefin metathesis reaction.

Since its discovery, three broad categories of this unique reaction have developed: (1) the exchange reaction, of which two types are known, productive and degenerate; (2) ring opening

metathesis polymerization (ROMP); and (3) degradation, also known as cyclization (Figure 1-2).³



i) Productive metathesis

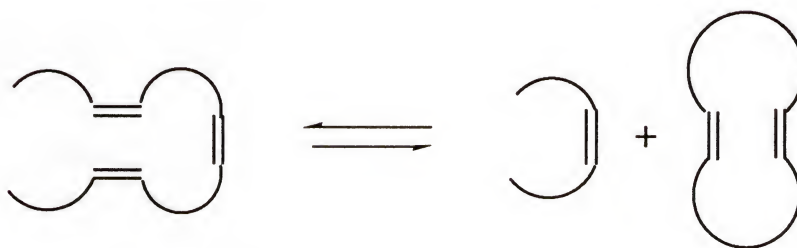


ii) Degenerate metathesis

a) Olefin exchange metathesis reaction



b) Ring opening metathesis polymerization



c) Degradation metathesis reaction

Figure 1-2. Illustration of the three categories of the olefin metathesis reaction.

Since cyclization metathesis chemistry can be considered as both the inverse of the ring opening metathesis reaction and an

intramolecular example of the exchange reaction, only categories (1) and (2) are discussed in detail in this introduction.

Figure (1-2a) illustrates the difference between the two types of exchange olefin metathesis reactions. The productive exchange reaction results in the formation of new olefins, while the degenerate exchange reaction trades the same olefinic unit between a pair of alkenes resulting in no net reaction. The terms disproportionation and transmetathesis are often utilized in further describing the exchange reaction. Disproportionation describes the reaction of an unsymmetric olefin with itself, while the transmetathesis reaction is between two different alkenes (Figure 1-3).

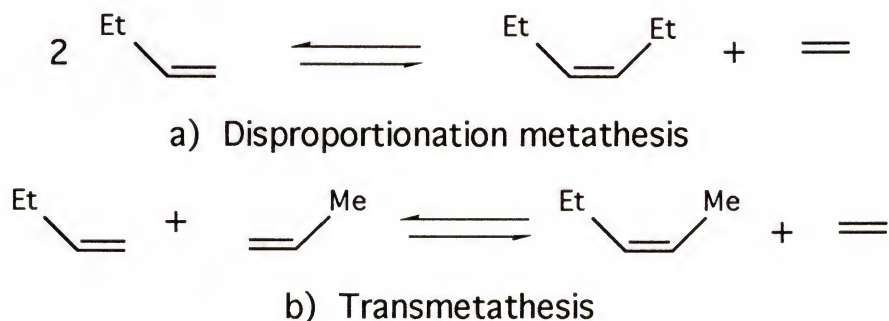


Figure 1-3. Illustration of the disproportionation and transmetathesis olefin metathesis reactions.

Historical Development of Olefin Metathesis Chemistry

The olefin metathesis reaction was introduced to the scientific community in 1960 with Truett's landmark publication detailing the ring opening metathesis polymerization of norbornene (Figure 1-4a).⁴ Four years passed before the exchange olefin metathesis reaction was reported by Banks,⁵ describing the

disproportionation of propene (Figure 1-4b). The commercial importance of these novel chemical processes was emphasized by the patent disclosures that preceded the respective publications by as much as four years.⁶

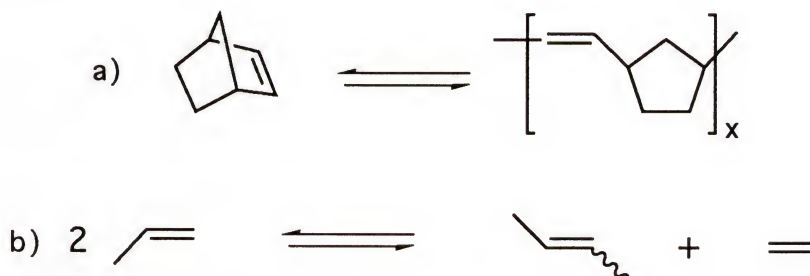


Figure 1-4. The first reported olefin metathesis reactions, a) the ring opening metathesis polymerization of norbornene,⁴ and b) the disproportionation of propene.⁵

Due to the differences in reaction conditions, the common basis of these two examples of olefin metathesis chemistry went unnoticed for several years. The gap that separated them was closed when Calderon, Ofstead and co-workers demonstrated that the same catalyst system could ROMP cyclooctene and cyclooctadiene,⁷ as well as disproportionate 2-pentene.^{2,8} It was at this point that ROMP and olefin exchange chemistry were first considered subsets of the same chemical reaction.

Classical Olefin Metathesis Catalyst Systems

It is not a coincidence that the early metathesis catalyst systems closely resemble Zeigler-Natta (Z-N) polymerization catalyst mixtures, since olefin metathesis chemistry evolved from

research aimed at improving the Zeigler-Natta polymerization reaction.⁹ In fact, there are several catalyst systems known that are capable of both Z-N chemistry (1,2-addition) and olefin metathesis. In an attempt to copolymerize ethene with cyclopentene, Natta discovered a catalyst system that alternates between the Z-N mechanism when reacting with ethene and the olefin metathesis mechanism when polymerizing the cyclic alkene, resulting in the unsaturated polymer illustrated in Figure (1-5a).¹⁰ Similarly, Hein reported a catalyst system that simultaneously polymerizes ethene via a Z-N mechanism and cyclopentene by a ROMP mechanism, resulting in the formation of the two homopolymers (Figure 1-7b).¹¹

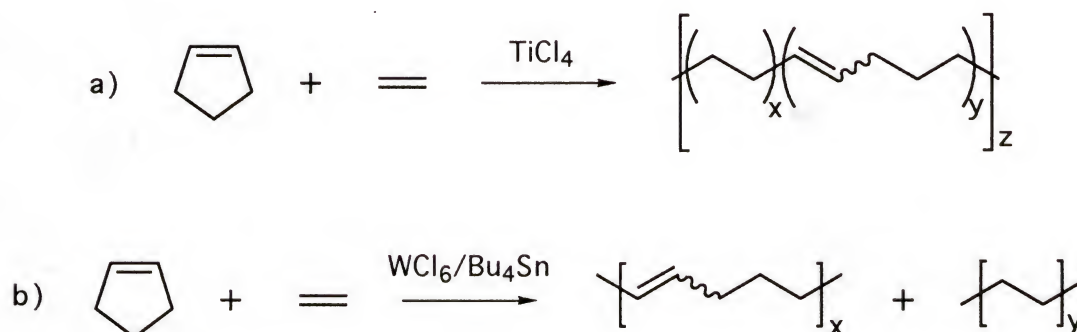


Figure 1-5. Examples of reactions that exhibit both ROMP and Z-N polymerization mechanisms from one catalyst system, a)¹⁰ and b)¹¹.

The olefin metathesis catalysts employed in the early stages of development of this relatively new chemical reaction are referred to as 'classical catalysts,' which can be heterogeneous, homogenous, or, as utilized for many industrial processes, supported catalysts.

The majority of the 'classical' olefin metathesis catalysts are based upon 11 transition metals: Ti, Zr, and Hf (group IVA); Nb and Ta (group VA); Mo and W (group VIA); Re (group VIIA); Ru and Os (group VIIA); and Ir (group VIII).^{3,9} The most effective catalysts have either Mo, W, or Re as the active metal center.

Characteristic of the classical catalyst systems is the use of a Lewis acid co-catalyst, most commonly based upon organometallic compounds of group I-IV elements, with alkyl complexes and metal halides of Li, Al, and Sn proving most popular.^{3,12} For example, typical classical metathesis catalyst systems include $\text{WCl}_6/\text{R}_4\text{Sn}$, $\text{MoCl}_2(\text{NO})_2\text{Cl}_2/\text{Me}_3\text{Al}$, $\text{WCl}_4/\text{Me}_4\text{Sn}$, and $\text{WCl}_6/\text{EtAlCl}_2$.

The Olefin Metathesis Mechanism

The search to understand the mechanism of the olefin metathesis reaction launched a multidisciplinary effort that would span more than 25 years, and is still an active area of research today. Ultimately it was the development of well defined catalysts that led to a clear understanding of this chemistry.

In 1964, Bailey and Banks provided the first evidence that the olefin metathesis reaction was reversible, as they observed that thermodynamic equilibrium concentrations of ethene and 2-butene were obtained in the disproportionation of propylene.⁵ Bradshaw and co-workers confirmed the reversibility of the olefin metathesis reaction by the generation of terminal olefins from the transmetathesis of ethene and various internal olefins (Figure 1-6), a process which became known as 'ethenolysis'.¹³

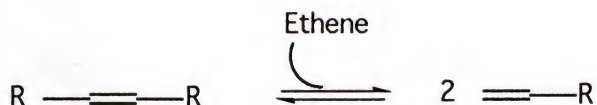


Figure 1-6. Reversibility of the olefin metathesis reaction demonstrated by the ethenolysis reaction.¹³

In 1967 Bradshaw suggested a quasicyclobutane intermediate in an attempt to explain the reaction products obtained from the metathesis disproportionation of propene (Figure 1-7), with the disclaimer that enough was not known about the olefin metathesis reaction to propose an actual mechanism.¹³

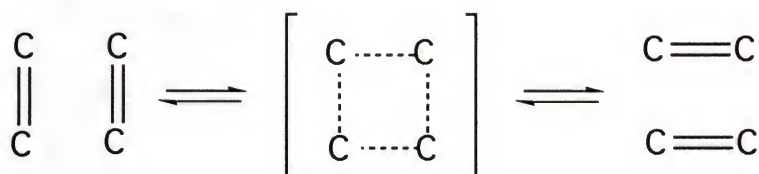


Figure 1-7. Bradshaw's quasicyclobutane intermediate proposed for the olefin metathesis reaction in 1967.¹³

While Natta originally proposed a mechanism which involved the cleavage of the alpha carbon-carbon σ bonds,¹⁴ Calderon, Ofstead *et al.* were the first to report a detailed investigation of the olefin metathesis mechanism.² These researchers, through the cleverly designed reaction of d₈-2-butene with 2-butene, proved that the double bond was completely broken during olefin exchange, a process referred to at the time as 'transalkylidienation', by demonstrating that the only new product formed was d₄-2-butene (Figure 1-8).⁸ This process was later confirmed for the olefin exchange reaction, and demonstrated to apply to the ring opening reaction as well.¹⁵⁻¹⁷

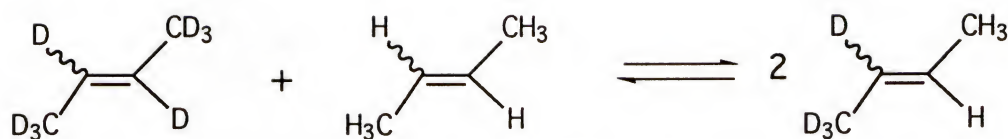


Figure 1-8. Olefin metathesis reaction that demonstrated the double bond was completely broken.⁸

Calderon proposed the first mechanism for the olefin metathesis reaction in 1968, drawing on the example of analogous and better understood reactions,^{18,19} as well as supporting theoretical considerations.²⁰ This mechanism, which became known as the 'pairwise mechanism', suggested the formation of a bisolefin-metal complex, followed by a four-centered transition state through which the 'transalkylidienation' took place through delocalized σ bonding (Figure 1-9). Calderon's mechanism, although later proven inaccurate, explained the metathesis reactions of the time so well that it gained general acceptance and later became the major obstacle to the recognition of the true mechanism.

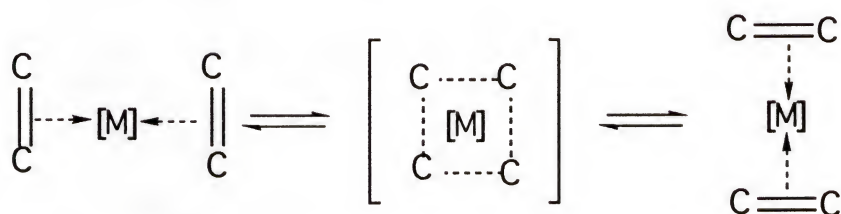


Figure 1-9. Pairwise mechanism as originally proposed by Calderon *et al.*⁸

The Metal Carbene Mechanism

The pairwise mechanism was so well established that when Herisson and Chauvin proposed an alternative mechanism in 1970, it

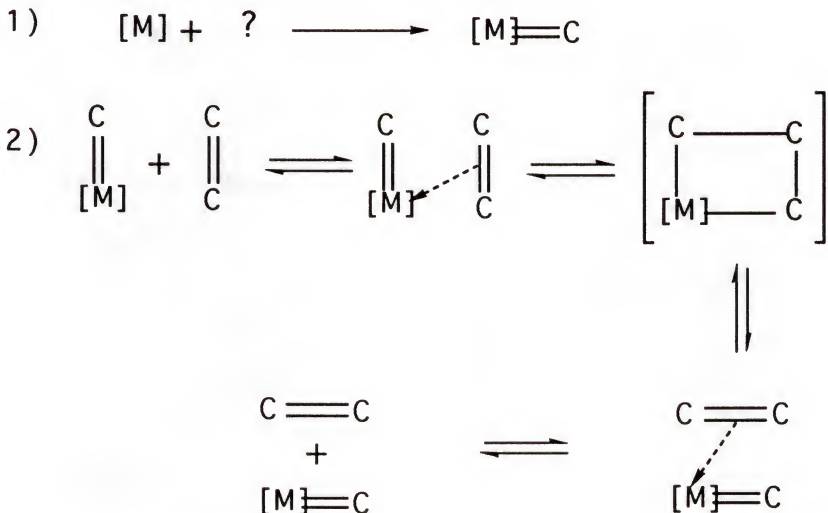


Figure 1-10. The metal carbene mechanism as proposed by Herisson and Chauvin in 1970.²¹

The first step of the metal carbene mechanism involves the formation of the metal-carbon double bond, known as a carbene or alkylidene. For the classical catalyst systems already discussed, alkylation of the transition metal followed by proton abstraction and elimination of an additional ligand, comprises the generally accepted process of carbene generation, and corresponds to step one of the metal carbene mechanism.¹² Figure (1-11) illustrates this process for a catalyst system studied by Grubbs in which the product methane was detected.²²

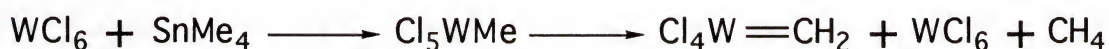


Figure 1-11. Carbene formation in a classical catalyst system.

The second step of the metal carbene mechanism (Figure 1-10) involves the formation of a metallacyclobutane from the reaction of an olefin with the metal carbene, which can then cleave to produce a new olefin. The olefin produced contains the atoms of the original alkylidene, while the newly generated alkylidene is comprised of atoms from the reacting olefin. The key feature of this mechanism, which distinguishes it from the pairwise mechanism, is the reaction of the carbene takes place with only one olefin at a time. Consequently, the metal carbene mechanism prognosticates a complete statistical distribution of products early in the reaction, whereas the pairwise mechanism predicts a statistical distribution only at equilibrium.

In fact, Herisson and Chauvin proposed the carbene mechanism in order to explain the statistical product mixture obtained essentially at 'time zero' for the transmetathesis of cyclopentene with 2-pentene (Figure 1-12).²¹ Early in the reaction, the pairwise mechanism dictates that only the C₁₀ product would be present.

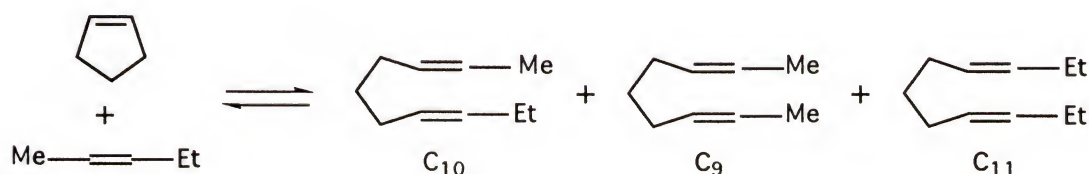


Figure 1-12. Transmetathesis reaction that led to the proposal of the carbene mechanism of olefin metathesis by Herisson and Chauvin.²¹

In retrospect, Chauvin's experiment appears to dispute the pairwise mechanism convincingly, but proponents of the already established mechanism rationalized Chauvin's results as a special

case of the pairwise mechanism, basing their arguments upon the kinetics of olefin-metal complex interchange.²³ Thus, while Chauvin's experimental evidence suggested an alternative mechanism was possible, it in no way refuted the pairwise mechanism, and sparked an argument that would last for more than 15 years. This debate fueled the vast research efforts investigating the olefin metathesis mechanism.²⁴

Additional support for the metal carbene mechanism was supplied by Katz and McGinnis in 1975 when the transmetathesis of a cyclic olefin was re-investigated, but this time two symmetric olefins were employed which emphasized the difference in the two opposing mechanisms (Figure 1-13).²⁵

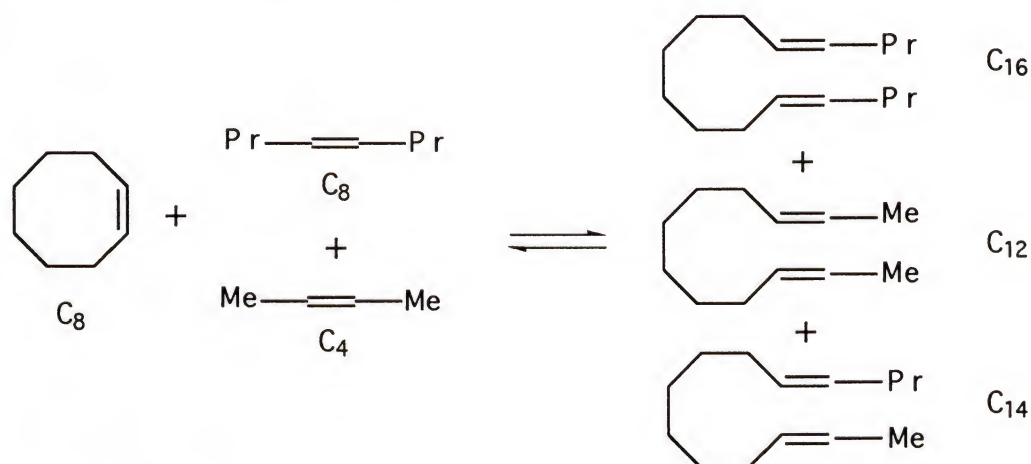


Figure 1-13. Transmetathesis reaction performed in order to distinguish between the pairwise and the carbene mechanisms.²⁵

Again, all product concentrations were extrapolated to 'zero time' and assumed to be the initially formed compounds. The carbene mechanism predicted a statistical mixture of all products,

while the pairwise supported the formation of the symmetric dienes, C₁₂ and C₁₆ only. The observed molar ratios C₁₄/C₁₂ = 1.34 and C₁₄/C₁₆ = 3.0 supported the carbene mechanism as the pairwise mechanism predicted values of zero for both of these ratios. While these findings were in favor of the carbene mechanism, the pairwise mechanism was still not disproven.

Inconclusive results were obtained from numerous elegant mechanistic studies that were based upon the reaction products. It became obvious that the debate over the true nature of the olefin metathesis reaction would not be resolved until the structure of the catalyst and the disputed reaction intermediates were defined and isolated.

In 1970, when Chauvin proposed the metal carbene mechanism, the only known stable carbene complexes did not function as olefin metathesis catalysts.^{26,27} By 1974, Schrock had reported several isolable carbenes (alkylidenes) that were prepared in a similar manner to the 'classical' olefin metathesis catalysts, yet these complexes were unreactive towards olefin metathesis.²⁶ It was difficult to say whether or not these findings had any bearing on the mechanistic debate.

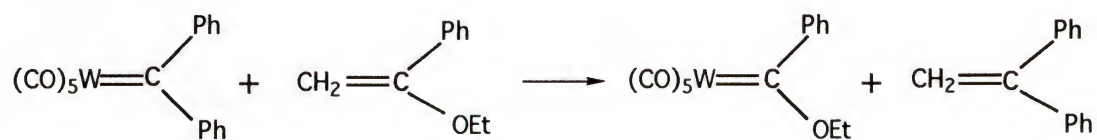


Figure 1-14. First olefin metathesis from an isolated carbene.²⁸

The ultimate support for the metal carbene mechanism came in 1974 when Casey prepared and isolated a carbene that showed

metathetic activity (Figure 1-14).²⁸ This reaction was the first demonstration of the carbene mechanism which substantiated the reaction between the olefin and the alkylidene was bimolecular (involving only one alkene), in obvious dispute of the pairwise mechanism. Katz expounded upon Casey's findings in 1976, when he demonstrated that the same carbene initiated the ROMP of cyclooctene with incorporation of the initial alkylidene atoms into the polymer chain (Figure 1-15).²⁹

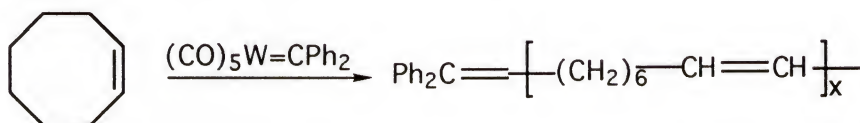


Figure 1-15. First ROMP with a well defined carbene, supporting the carbene mechanism.²⁹

Further support of the metal carbene mechanism came from Tebbe's reported olefin metathesis of methylenecyclohexane with what is now referred to as Tebbe's reagent ($\text{Cp}_2\text{TiCH}_2\text{Me}_2\text{AlCl}$).³⁰ Tebbe was able to demonstrate the exchange of olefins catalyzed by this carbene, as well as isolate the carbene at the end of the reaction (Figure 1-16). Grubbs *et al.* filled in the rest of the the

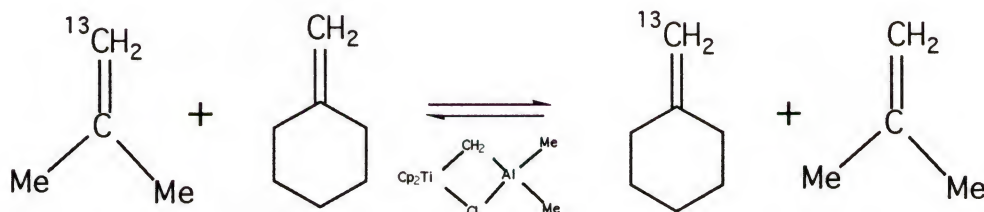


Figure 1-16. First olefin metathesis reaction where the carbene was isolated at the end of the reaction.³⁰

catalytic cycle when they isolated the metallacyclobutane from an olefin metathesis reaction and showed that the metallacycle was capable of catalyzing olefin metathesis.³¹

Kress and co-workers were the first to observe the metal carbene and metallacyclobutane of a catalytic olefin metathesis polymerization simultaneously by proton NMR, thus drawing the connection between all species originally proposed by Chauvin for the olefin metathesis mechanism over 15 years earlier.³²

The metal carbene mechanism is now the generally accepted mechanism for the olefin metathesis reaction and ongoing research efforts continue to define the details of this chemical reaction.

Development of a Lewis Acid Free Metathesis Catalyst

The investigations into the mechanism of the olefin metathesis reaction led researchers away from the poorly defined and less understood 'classical' catalyst systems and in the direction of well defined metal alkylidenes capable of catalyzing the olefin metathesis reaction. Whereas the work of Fischer,²⁷ Tebbe,³⁰ Casey,²⁸ Grubbs,³¹ and Osborn³³ proved instrumental in the development of the metathesis mechanism, the alkylidenes utilized demonstrated poor catalytic activity.

Initial work by Schrock *et al.* resulted in the synthesis of stable carbene complexes of tungsten that were well characterized, but retained the 'classical' catalytic nature as they required a Lewis acid co-catalyst to affect olefin metathesis.³⁴ In 1986, Schrock reported a four coordinate d^0 tungsten alkylidene capable of

catalyzing the olefin metathesis reaction at rapid rates without a Lewis acid co-catalyst (Figure 1-17).³⁵

In an elegant study, Schrock demonstrated that control over the metathesis activity of this catalyst could be achieved by careful tuning of the electronic and steric properties of the alkoxide ligands.³⁶ The metathesis activity of the catalyst increased with the increased fluorine substitution of the tert-butoxide ligand (OR), where R was varied among $\text{C}(\text{CH}_3)_3$, $\text{C}(\text{CH}_3)_2(\text{CF}_3)$, and $\text{C}(\text{CH}_3)(\text{CF}_3)_2$.

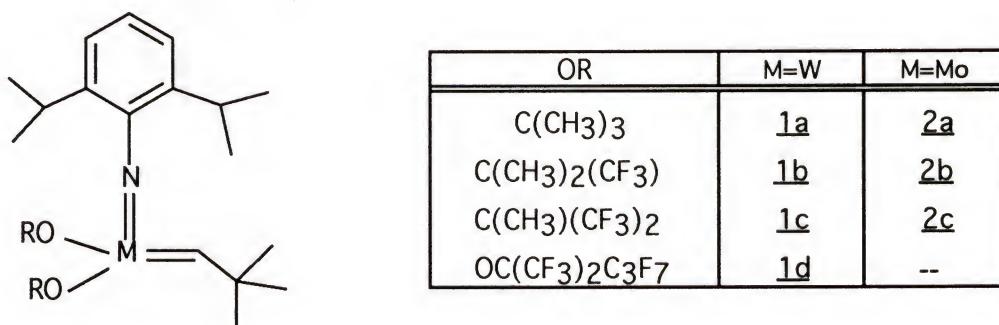
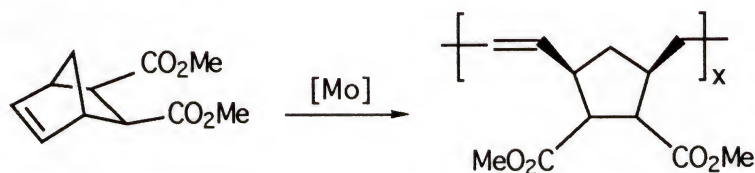


Figure 1-17. First reported highly active Lewis acid free olefin metathesis catalyst 1c.³⁵

The increased reactivity was attributed to the increased electrophilicity of the metal center, which allowed the catalyst to overcome the steric interactions involved in the formation of the metallacyclobutane intermediate. The size of the alkoxide was shown to play an important role in determining the activity of these catalysts, since the catalytic activity decreased when $\text{OC}(\text{CF}_3)_2\text{CF}_2\text{CF}_2\text{CF}_3$ was the alkoxide.



- a) Deactivation of tungsten based catalysts 1a-c through a Wittig type reaction with an ester.



- b) ROMP of ester functionalized norbornene with the molybdenum based catalyst, where [Mo] represents catalyst 2a.

Figure 1-18. Illustration of the differences in polar group tolerance exhibited by the tungsten and molybdenum based Lewis acid free metathesis catalysts.

Although varying the alkoxide allowed for some control over the catalytic activity, many polar functionalities could not be tolerated. The tungsten catalysts 1a-c readily react in a Wittig type manner with ester groups which results in deactivation of the catalyst as the tungsten oxide is formed (Figure 1-18a).³⁵ Catalyst tolerance to polar functionalities has been an inherent problem in olefin metathesis chemistry, since the Wittig type behavior is preceded for metathesis catalysts based upon Ta, Ti, and Zr.³⁷⁻³⁹ Increased control over the catalyst activity was gained by changing the metal center as the series of molybdenum catalysts 2a-c was reported in 1987.⁴⁰ The less electrophilic molybdenum catalysts 2a-c demonstrate a lower metathetic activity but higher selectivity, and consequently they cleanly metathesize ester containing olefins (Figure 1-18b).⁴¹ Both the tungsten and molybdenum based catalysts produce olefins from aldehydes, a

phenomenon which has been exploited as a ROMP endcapping reaction.⁴²

The highly selective molybdenum catalysts have allowed numerous functional groups to be incorporated into ROMP polymers; ether, thioether, ester, amide, nitrile, and metal containing monomers have all been polymerized through ROMP techniques.⁴³

The development of these highly active, well defined Lewis acid free metal alkylidene olefin metathesis catalysts has opened doors to the study of the olefin metathesis reaction in greater detail than was previously possible, and has led to a better overall understanding of the olefin metathesis reaction; numerous catalyst intermediates have been observed and in many cases isolated. Undoubtedly, further developments in catalyst research will bring about an increased degree of control over the olefin metathesis reaction, thus augmenting the importance of this valuable synthetic tool.

Olefin Metathesis Polymerization

For more than twenty-five years, ring opening metathesis polymerization defined the application of olefin metathesis reaction to polymer synthesis, but more recently the development of a new polymerization scheme utilizing the exchange olefin metathesis reaction has been developed, namely acyclic diene metathesis (ADMET).⁴⁴ The general scheme for the ROMP chemistry was presented in an earlier section as one of the three main categories of the olefin metathesis reaction. In this section, ROMP and ADMET

chemistry are discussed in greater detail to allow for a clear comparison of the two polymerization techniques.

Ring Opening Metathesis Polymerization



Figure 1-19. Illustration of a ROMP reaction, demonstrating that the polymer repeat unit contains one less ring than the monomer.

Ring opening metathesis polymerization is chain growth chemistry which occurs through the conversion of mono- and polycyclic alkenes into linear polymer whose repeat units contain one less ring (Figure 1-19).⁴⁵ As with all olefin metathesis chemistry, ROMP reactions are equilibrium processes with an ideal reaction establishing an equilibrium between linear polymer and cyclic monomer.⁴⁶ Since the total number and type of bonds remains unchanged from monomer to polymer, with the exception of cis/trans isomerization, the enthalpy change (ΔH) for the polymerization reaction is primarily a function of monomer ring strain. The release of the ring strain is the principle driving force that shifts the equilibrium in favor of the polymer for most ROMP reactions, especially for highly strained bicyclo-monomers. However, the release of ring strain is not a requirement, as the polymerizability of a cyclic monomer is a function of both enthalpy (ΔH) and entropy (ΔS) changes.

Ring strain is required for the attainment of high molecular weight polymer for monocyclic rings of 8 or less carbon atoms since polymerization entropy changes are unfavorable.⁴⁴ ROMP is highly favorable energetically for 3, 4, and 8 membered rings, and high molecular weight polymers are readily obtained from such monomers. Significant amounts of monomer remain at equilibrium in the ROMP reactions of cyclopentene and cycloheptene due to relatively low monomer ring strain; however, the equilibrium can be shifted in favor of polymer by lowering the temperature of the reaction.⁴⁷ In fact, cyclohexene has been shown to ring open at sufficiently low temperatures.⁴⁸

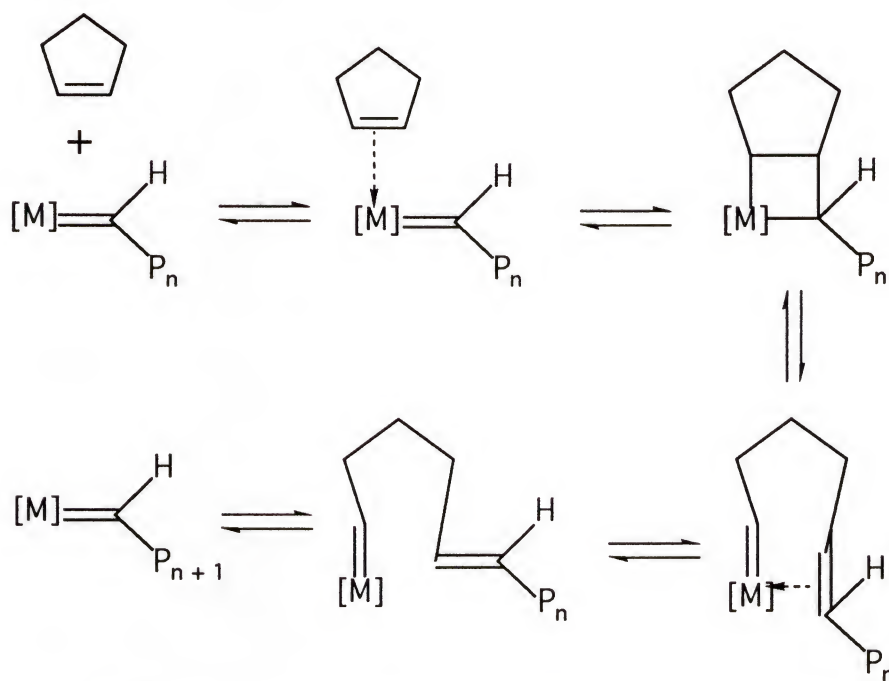


Figure 1-20. Mechanism for the ring opening metathesis polymerization reaction, illustrated for cyclopentene.

For large cyclic olefins the translational entropy (ΔS) gained from the conversion of monomer to polymer provides the driving

force for the reaction of strain free rings ($\Delta H \cong 0$). For example, the 24 carbon cyclic trimer of cyclooctene has been polymerized via ROMP techniques.⁴⁹

The steps of the ROMP mechanism are outlined in Figure (1-20) for the polymerization of cyclopentene. The catalyst is a transition metal alkylidene (carbene) represented by $[M]$ where 'P' represents the polymer chain, and the brackets around 'M' indicate additional ligands are present. During propagation the monomer coordinates to the metal in a pi complex which leads to the formation of the metallacyclobutane intermediate. The metallacyclobutane then cleaves to produce the new pi complex where the polymer chain is increased by one monomer unit. Olefin exchange to form the monomer pi complex resets the catalytic cycle.

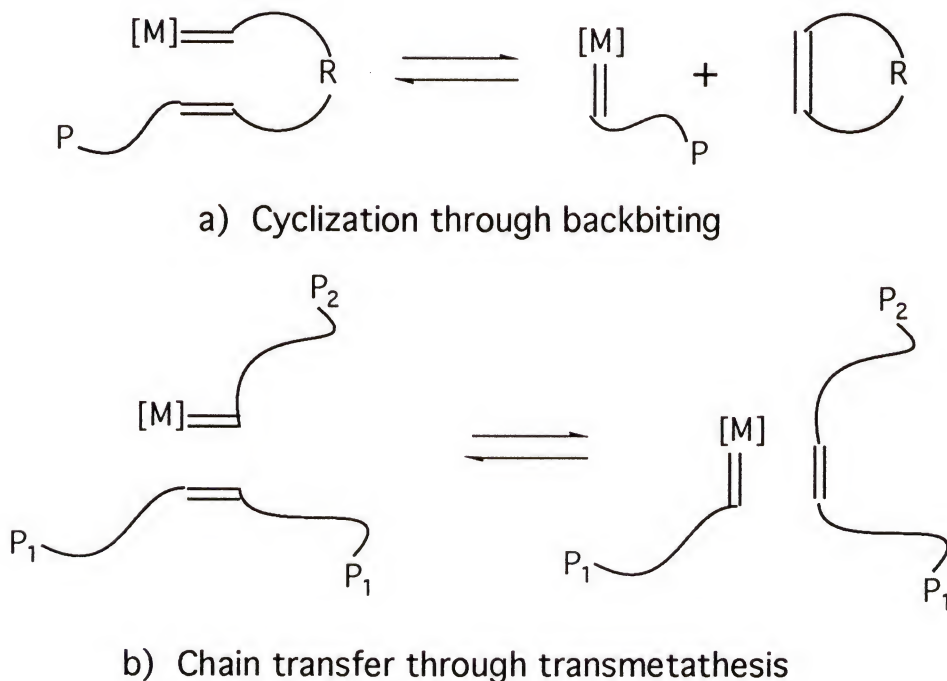


Figure 1-21. Secondary metathesis reactions in ROMP chemistry.

The mechanism implies that ROMP is a 'living' polymerization reaction since the catalyst remains attached to the growing end of the polymer chain. However, the living nature is destroyed by side reactions often present in ROMP chemistry. Since the olefin functionality remains in the polymer chain, secondary metathesis reactions lead to cyclic oligomers and chain transfer (Figure 1-21). The presence of the competing metathesis reactions manifests as broad molecular weight distributions for the resulting polymer.

The development of Lewis acid free olefin metathesis catalysts has brought about a renaissance for ROMP chemistry, as control over the activity of the catalyst has resulted in controlled polymer synthesis. Grubbs reported the first 'living' ROMP with the polymerization of norbornene with a heat generated titanium alkylidene.⁵⁰ Grubbs demonstrated a linear increase in molecular weight proportional to the catalyst concentration with subsequent additions of monomer, with the polydispersities of the polymers produced as low as 1.08. Additionally, the living chain end, an alkylidene, was characterized by ^1H NMR. Thus, all of the requirements for a living polymerization system were met: narrow and controlled molecular weight of the polymer, high efficiency in catalysis, an absence of chain transfer and termination reactions, and characterizable chain-carrying intermediates.⁵¹

The highly active olefin metathesis catalysts developed by Schrock have also demonstrated the ability to polymerize norbornene and functionalized norbornenes in a living nature.⁵² The living nature of this polymerization system has been exploited for the synthesis of a number of well characterized block and graft

copolymers.⁵³ The scope of applications of ROMP chemistry has been expanded as a direct consequence of the increase in control over the polymer structure. Advances in catalyst development are responsible for this growth with the work of Schrock and Grubbs proving instrumental.

Acyclic Diene Metathesis (ADMET) Polymerization

Perhaps the most significant consequence that can be attributed to the highly active olefin metathesis catalysts developed by Schrock is the evolution of a new polymerization method, ADMET.⁵⁴ This new polymerization methodology is the focus of this dissertation; thus, the important aspects are introduced for clarity.

The potential application of the olefin metathesis reaction to the polymerization of acyclic dienes was perceived and attempted as early as 1970, but with little success.^{55,56} The first reported attempt at ADMET polymerization employed 1,5-hexadiene **3** but only low molecular weight oligomers (< 500 gm/mol) were attained under the reaction conditions which included a Lewis acid co-catalyst (Figure 1-22).

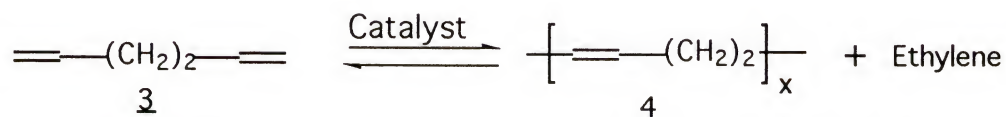


Figure 1-22. General ADMET polymerization reaction scheme.

This reaction received little attention until 1987 when Lindmark-Hamberg and Wagener re-investigated the polymerization

of 1,5-hexadiene 3 with a $\text{WCl}_6/\text{EtAlCl}_2$ catalyst system.⁵⁷ Through careful analysis of the reaction products the metathesis reaction was shown to be the prominent reaction, but low molecular weight oligomers represented the extent of the polymerization. In addition to the metathesis products an insoluble solid was also produced, suggesting competing side reactions.

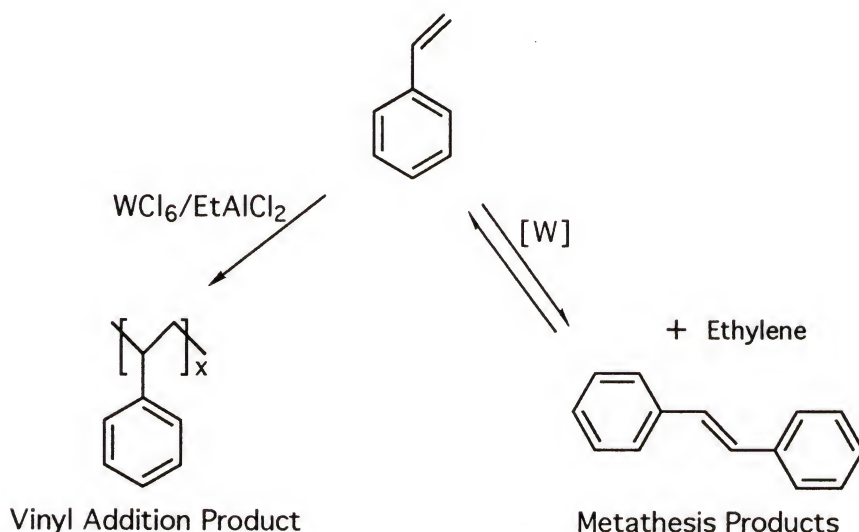


Figure 1-23. Difference in reaction pathways demonstrated by the 'classical' catalyst ($\text{WCl}_6/\text{EtAlCl}_2$) and the Lewis acid free metathesis catalyst $[\text{W}]$ 1c.^{57,58}

Through an elegant model reaction with styrene as the olefin, Wagener was able to demonstrate that the main factor limiting the polymerization process was the competing vinyl addition reaction.⁵⁸ The addition of styrene to the catalyst mixture ($\text{WCl}_6/\text{EtAlCl}_2$) produced polystyrene with no evidence for the metathesis reaction (Figure 1-23).

Concluding that the acidity of the catalyst system was responsible for the side reactions Wagener *et al.* turned their

attentions to Schrock's Lewis acid free metathesis catalyst, reported just one year prior.³⁵ Employing catalyst 1c styrene was quantitatively converted into stilbene (Figure 1-23). Elimination of the acid co-catalyst successfully eliminated the vinyl addition side reaction.⁵⁸

Without the detriment of competing side reactions, the research effort concentrated on polymer synthesis. The successful polymerization of 1,9-decadiene 5 to polyoctenamer 6 with catalyst 1c (Figure 1-24)⁵⁷ was the first example of ADMET polymerization, achieved just 19 years after its inception.^{54,58,59} The polymerization of 1,5-hexadiene 3 to 1,4-polybutadiene 4 quickly followed (Figure 1-22).^{54,60}

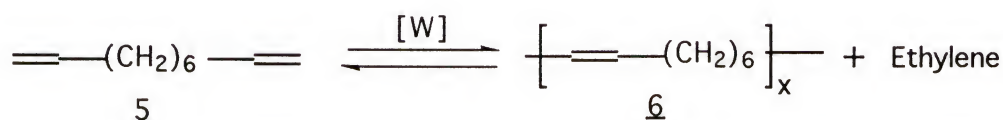


Figure 1-24. The first successful ADMET polymerization, where [W] represents catalyst **1c**.⁵⁹

Acyclic diene metathesis polymerization is an example of the olefin metathesis exchange reaction with the complete catalytic cycle involving two such reactions.⁵⁴ The ADMET polymerization cycle is illustrated in Figure (1-25), where 'M' represents the transition metal of the active catalyst while the brackets around 'M' denote the additional coordinated ligands.

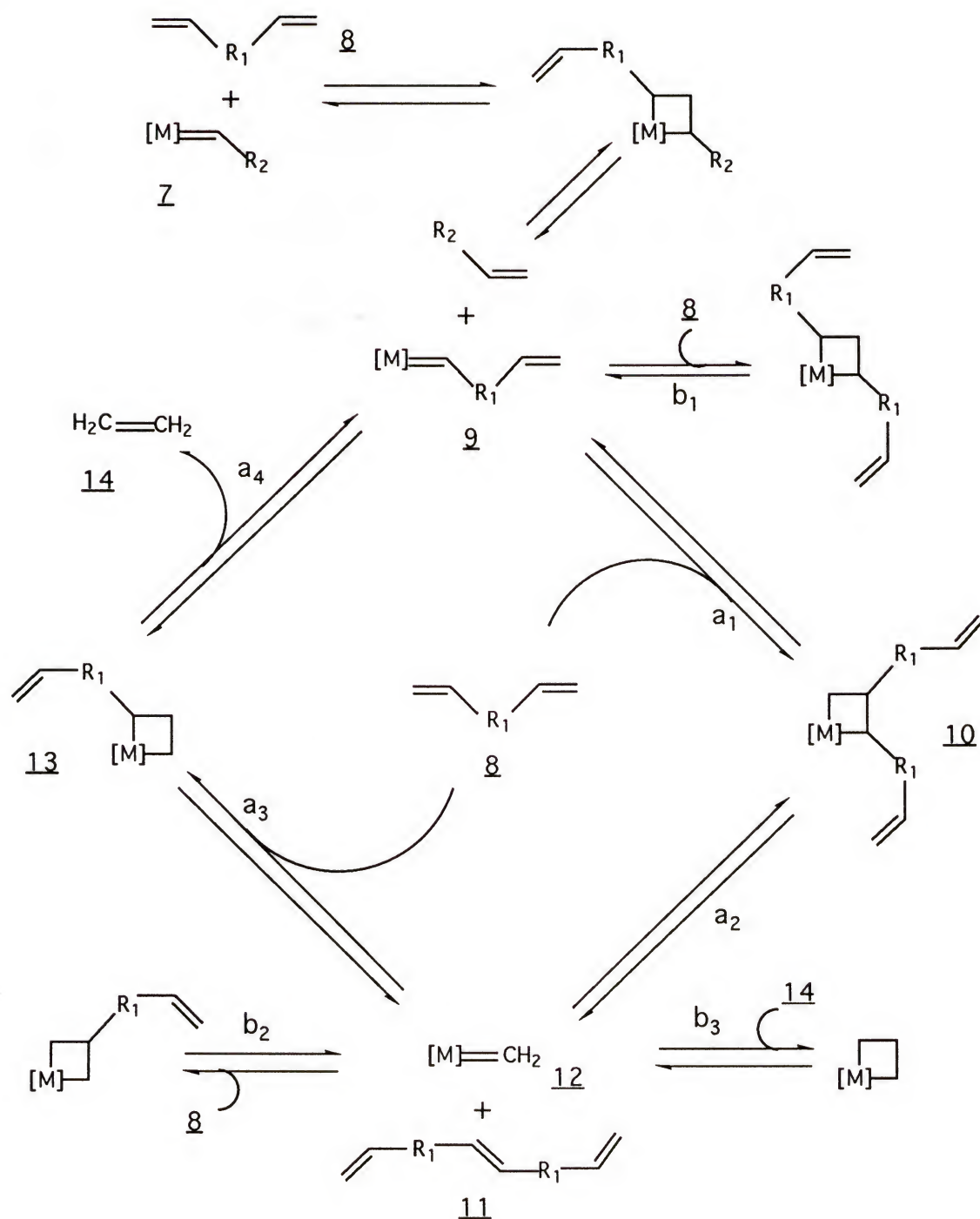


Figure 1-25. The ADMET polymerization cycle.⁵⁴

The initial alkylidene Z reacts with the diene monomer 8 to form the difunctional alkylidene-olefin species 9 which begins the catalytic cycle. Advancing clockwise, along pathways a_1 and a_2 , the

productive metathesis with another monomer (n-mer) proceeds through the α,β -disubstituted metallacycle 10 which can release the dimer 11 ([n+1]-mer) and the only true catalytic species, the methyldiene 12. Reaction of the methylene alkylidene with another diene (n-mer) along pathway a_3 results in the α -monosubstituted metallacycle 13 which upon cleavage regenerates the difunctional alkylidene-olefin species 9 and releases the condensate monoene, which is ethene 14 in this illustration.

The degenerate (non-productive) exchange reactions, pathways b_1 , b_2 and b_3 , slow the overall rate of polymerization but are not detrimental to polymer formation. As is illustrated in the ADMET polymerization cycle, molecular weight increases are only observed when the terminal olefins are coupled; therefore, the transmetathesis reaction (Figure 1-26) serves only to randomize the molecular weight distribution, and equilibrate the cis/trans ratio.

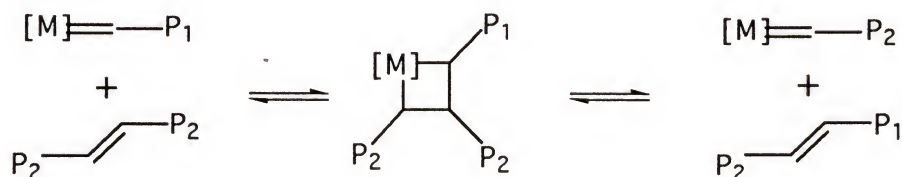


Figure 1-26. Transmetathesis during ADMET polymerization reaction resulting in randomization of the molecular weight.

In contrast to the ROMP mechanism, the catalyst metal center is dissociated from the polymer chain during an ADMET polymerization, which constitutes the step nature of this polymerization reaction. The metathesis of acyclic dienes is an equilibrium process that is driven in favor of the polymer by

removal of the monoene condensate. The reversibility of this process has been demonstrated by the lowering of the molecular weight of polymer through ethenolysis chemistry.⁶¹⁻⁶⁴

The step condensation nature of ADMET polymerizations clarifies the relative failure of early attempts at polymer formation. Step polymerizations proceed through the slow build-up of low molecular oligomers until nearly all of the functional groups have been consumed; thus high molecular weight polymer is not produced until late in the reaction. The number average degree of polymerization (\bar{X}_n) for a step polymerization is defined by the extent of conversion of functional groups (ρ) and the balance of stoichiometry according to the following equation:

$$\bar{X}_n = (1 + r) / (1 + r - 2\rho) \quad \text{Eqn. (1-1)}$$

where r is the stoichiometric imbalance ratio ($r \leq 1$), and ρ is the extent of conversion expressed as the fraction of functional groups consumed. For pure dienes, the stoichiometric ratio is unity and the equation simplifies to the Carothers equation:

$$\bar{X}_n = 1 / (1 - \rho) \quad \text{Eqn. (1-2)}$$

A simple plot of \bar{X}_n versus ρ illustrates that conversions greater than 99% are required for polymer formation (Figure 1-27).⁶⁵

The presence of competing side reactions severely limit the molecular weight of a step polymer. The vinyl addition chemistry observed by Lindmark-Hamberg and Wagener was most likely responsible for the failure of the early attempts at ADMET

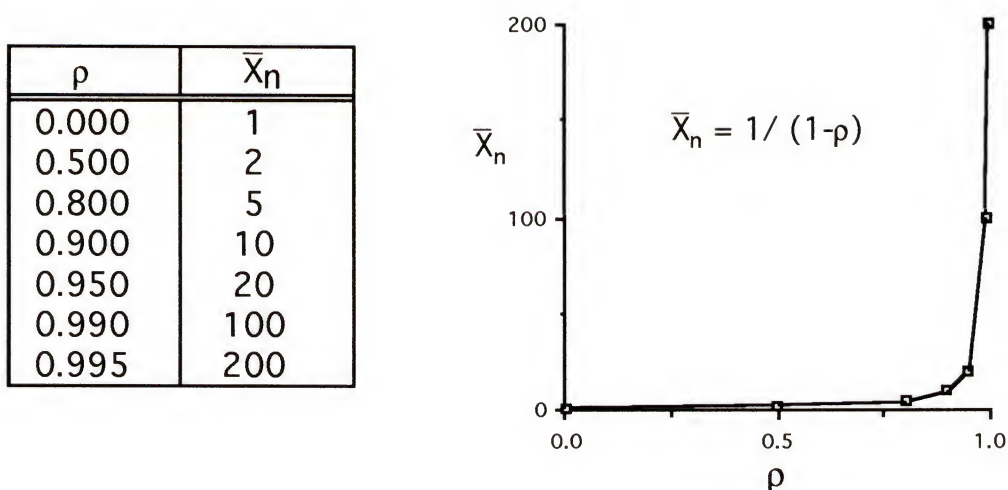


Figure 1-27. Plot of Carothers equation illustrating that polymer is produced only at conversions exceeding 99%.

polymerizations with Lewis acid co-catalysts.⁵⁸ Whereas the utilization of a Lewis acid free metathesis catalyst successfully eliminated the detrimental side reactions, optimization of the reaction conditions were required to afford high molecular weight polymers via ADMET chemistry.



Figure 1-28. Equilibrium reaction of the dimerization of butene to hexene and ethene. Equilibrium value is based upon the gas phase thermodynamic data for each species.^{66,67}

The low equilibrium value associated with ADMET polymerizations can be estimated from the thermodynamic data available for butene, 3-hexene, and ethene.^{66,67} The metathesis dimerization of butene models the basic reaction associated with ADMET polymerizations, and demonstrates that although the forward

reaction is spontaneous, equilibrium is established at 24% conversion (Figure 1-28). If this same equilibrium value is applied to polymerizations of α,ω -dienes the number average degree of polymerization (\bar{X}_n) predicted is 1.3. Therefore, ADMET reactions are driven entropically to completion by removal of the monoene condensate, usually ethene. For this purpose, ADMET polymerizations are generally carried out on a vacuum line to facilitate the removal of the monoene, but also to exclude water and oxygen, potential catalyst poisons.^{58,59}

Unlike ROMP chemistry, ADMET reactions are generally performed in the absence of solvent in order to minimize cyclization and afford favorable polymerization kinetics. Current catalyst sensitivity limits the upper reaction temperature to 55 °C.⁵⁹ Undoubtedly, future catalyst developments will lift this restriction.

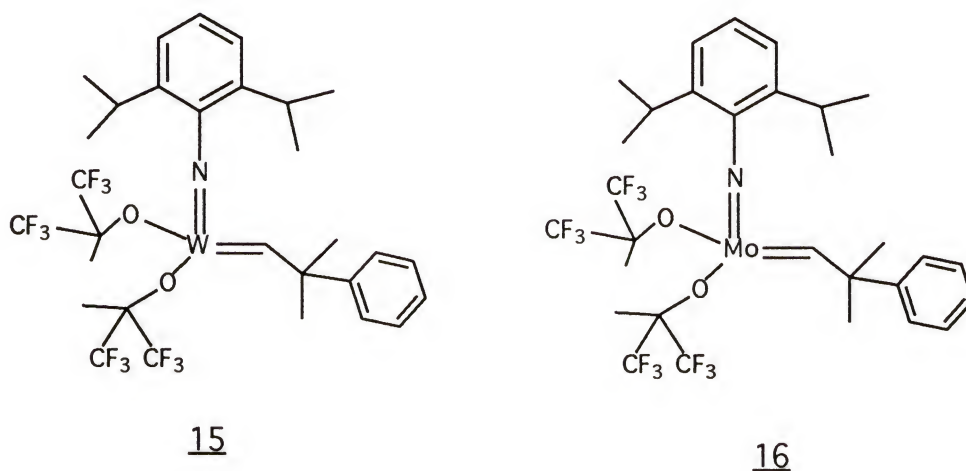


Figure 1-29. Lewis acid free metathesis catalysts currently employed in ADMET polymerizations.^{35,36}

Currently, the two common catalysts employed for the ADMET polymerizations are illustrated in Figure (1-29). The neopentylidene

of catalyst 1c has been replaced with a neophylidene as a synthetic convenience. The molybdenum catalyst 16 exhibits an increased rate of polymerization over the tungsten version 15, but more importantly, maintains the higher degree of tolerance towards polar functionalities demonstrated in ROMP polymerizations.⁶⁸ Dienes containing oxygen,⁶⁹⁻⁷¹ sulfur,⁷² hindered ketones,⁷³ esters,^{74,75} carbonates,^{76,77} and siloxanes⁷⁸⁻⁸¹ have all been polymerized with catalyst 16. Potential coordination of lone electron pairs requires that these groups be separated from the reacting olefin by several atoms.⁶⁸

The relative spacing of the dienes is equally important, as monomers capable of cyclization to six-membered rings, i.e. 1,7-octadiene, are avoided due to the unfavorable equilibrium between the cyclized product and the polymer. Additionally, monomers that can form five-membered rings have been polymerized, but as in ROMP polymerizations, there is a temperature dependent equilibrium between the polymer and cyclic product.⁷⁰ Since ring strain is not a consideration for ADMET monomers, many polymer structures attainable through ADMET chemistry are not accessible via ROMP techniques.

Structure Reactivity Study

Since the discovery of the olefin metathesis reaction, numerous studies investigating the relationship between the structure and the metathetic activity of various hydrocarbons have been reported, with the metathesis reactions of mono-enes often used to probe the mechanism of this unique reaction.³ Essentially

all of the previous studies have utilized a classical catalyst system, one that contains a Lewis acid co-catalyst, which at the time, was all that was available in terms of an active metathesis catalyst. However, acyclic diene metathesis polymerizations require the use of a Lewis acid free catalyst,⁴⁴ and to date, only two such catalysts have been successfully employed to this new step condensation chemistry, $W(CHCMe_2R)(N-2,6-C_6H_3-iPr_2)-[OCCH_3CF_3)_2]_2$ and $Mo(CHCMe_2R)(N-2,6-C_6H_3-iPr_2)[OCCH_3CF_3)_2]_2$. Since this dissertation focuses on developing the relationship between the structure of the olefins and their metathetic activity as it pertains to the ADMET polymerization of hydrocarbon monomers, the structure reactivity studies were performed with catalysts 15 and 16 exclusively.

Chapter 2 addresses the chemistry associated with the ADMET copolymerization of two monomers possessing the same functionality. The random copolymerization predicted by the step nature of the ADMET mechanism is investigated in detail. The reactivity relationship for substituted hydrocarbon olefins is the focus of Chapters 3 and 4. While the former details the steric influence associated with direct substitution of the olefin functional group, the latter concentrates on substitution at the allylic carbon. Whereas model compound studies are often employed (reactions of monoenes), the goal of this research has been to define the relationship between the structure of the hydrocarbon olefins and their metathetic activity as it applies directly to ADMET polymerization chemistry. Each chapter contains examples of how

the knowledge gained from the model compound studies were applied to ADMET polymer synthesis.

CHAPTER 2

COPOLYMERIZATION OF 1,5-HEXADIENE AND 1,9-DECADIENE

The success of acyclic diene metathesis (ADMET) polymerization has opened a new chapter in polymer chemistry. Although the pioneering homopolymerizations of 1,9-decadiene and 1,5-hexadiene were significant, it was important to broaden the scope of this new synthetic technique beyond the formation of known polymers, and considering the tremendous significance of copolymers in polymer science, the logical continuation of ADMET research was the copolymerization of these two monomers. Herein is reported the first copolymerization performed via ADMET, and the subsequent preparation of a series of previously unknown copolymers synthesized with the same techniques.⁸²

If the reactivities of all functional groups in a step condensation polymerization are identical, irrespective of the length of the molecule to which they are attached, then the comonomers become randomly distributed along the polymer chain in amounts proportional to their concentrations in the monomer feed.⁸³ Since acyclic diene metathesis polymerization is a step-condensation polymerization,⁵⁹ the transmetathesis reaction (Figure 2-1), where a monomer is inserted into a growing polymer chain, should randomize any copolymer produced from 1,5-hexadiene and 1,9-decadiene. The tungsten catalyst 15 employed for these

copolymerizations has a reported preference for the transmetathesis reaction.⁸⁴

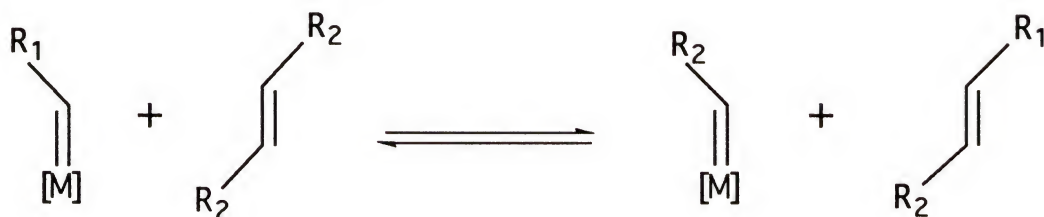


Figure 2-1. Illustration of the transmetathesis reaction showing the exchange of olefin substituents.

Random Copolymer Synthesis

The first copolymer produced by ADMET polymerization employed an equimolar mixture of 1,9-decadiene 5 and 1,5-hexadiene 3 in a premixed monomer feed (Figure 2-2). Four different monomer feed ratios were applied to produce four copolymers; the monomer feeds consisted of a range of ratios from 5 to 75 mole % 1,5-hexadiene (Table 2-1).

It was necessary to demonstrate that the polymers synthesized from the comonomer feeds were copolymers containing both monomers in the same polymer chain, and not merely blends of the two homopolymers. The homopolymer of monomer 5, which is polyoctenamer 6, is a crystalline polymer that readily precipitates from toluene as a white granular powder when added to methanol, while the homopolymer of monomer 3, 1,4-polybutadiene 4, precipitates as an amorphous solid when the molecular weight is in the range produced for ADMET polymers. If the copolymerization

Table 2-1. Predetermined Copolymer Monomer Feed Ratios.			
Copolymer	1,9-deca- diene (mmol)	1,5-hexa- diene (mmol)	Ratio 1,9:1,5 (Dienes)
17	6.62	6.34	50:50
18	8.95	2.95	75:25
19	10.10	0.55	95: 5
20	3.70	11.10	25:75

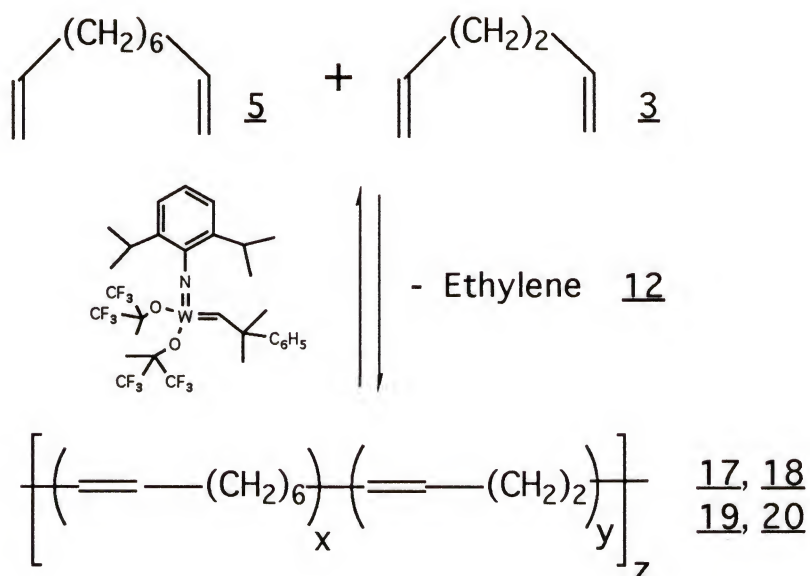


Figure 2-2. Copolymerization reaction of 1,9-decadiene 5 with 1,5-hexadiene 3 from a pre-mixed monomer feed resulting in a random copolymer.

reactions had produced a blend of two homopolymers, precipitation of these blends would have resulted in at least partial separation of the two homopolymers. The polymers 17, 18, 19, and 20 all precipitated as uniform materials, suggesting that copolymers had been synthesized.

Analysis of these new ADMET copolymers by size exclusion chromatography (SEC) showed one uniform peak for each polymer, with a polydispersity index (PDI) approaching the expected value of 2.0.^{85,86} This data is consistent with the synthesis of copolymers since two homopolymers would be expected to produce a bimodal distribution, or at least disturb the distribution in the SEC enough to produce an unexpected value for the polydispersity index. The molecular weights calculated for copolymers 17, 18, 19, and 20 were within the expected range for ADMET polymers (Table 2-2).

Table 2-2. Molecular Weight Analysis of Copolymers Synthesized via the ADMET Polymerization of 1,9-Decadiene <u>6</u> and 1,5-Hexadiene <u>3</u> .				
Polymer	\bar{M}_n (SEC) ^a (x 10 ³)	\bar{M}_n (VPO) ^b (x 10 ³)	PDI ^c	$[\eta]$ ^d
<u>17</u>	8.1	8.0	1.9	0.30
<u>18</u>	12	12	2.0	0.35
<u>19</u>	7.7	8.0	1.9	0.28
<u>20</u>	9.6	9.8	1.9	---
a) Size Exclusion Chromatography, relative to polybutadiene standards (gm/mol) b) Vapor Pressure Osmometry, calibrated with sucrose octaacetate, (gm/mol) c) Polydispersity Index from SEC, \bar{M}_w/\bar{M}_n d) Intrinsic Viscosity measured in toluene at 25 °C, (gm/ dL)				

Determination of Copolymer Composition by Proton NMR

Analysis of polymers 17, 18, 19 and 20 by ¹H NMR provided information about the ratios of monomers incorporated into these copolymers. Since the reaction procedure involved exposing the contents of the reaction flask to intermittent high vacuum, it could

not be assumed that the monomer ratio in the polymer matched the monomer feed ratio. It was necessary to be able to determine the monomer ratio of the actual polymer produced, and to show that the monomer feed had been maintained throughout the reaction.

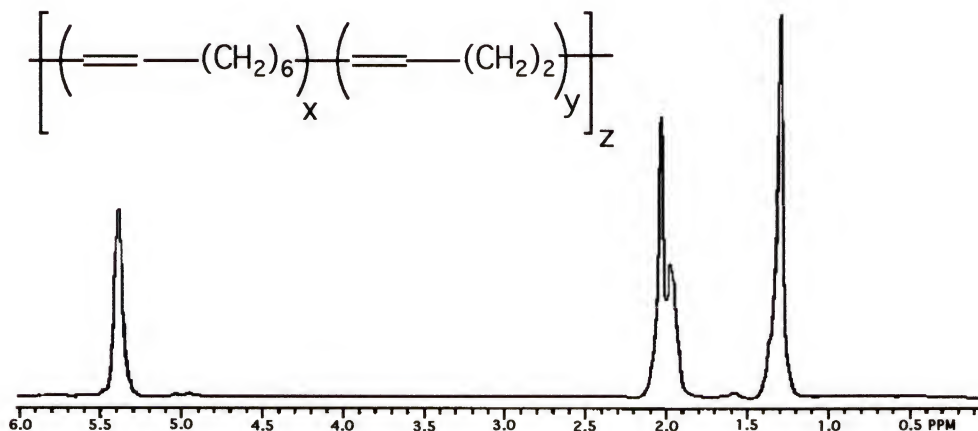


Figure 2-3. ^1H NMR of 50:50 monomer feed copolymer 17.

The overlapping proton signals centered at 2.1 ppm correspond to the methylene protons, from both the 1,9-decadiene 5 and the 1,5-hexadiene 3 monomers, that are adjacent to the olefin, which represents 4 protons per monomer unit (Figure 2-3).⁸⁷ The proton signal at 1.30 ppm corresponds to the other 8 methylene protons in the 1,9-decadiene monomer unit alone. By integration of these two proton signals, the monomer ratio present in each of the polymers, 17, 18, 19 and 20, was determined according to Equations (2-1) and (2-2) :

$$(I_{2.1}/4) - (I_{1.3}/8) = \text{rel.\# 1,5-hexadiene units} \quad \text{Eqn. (2-1)}$$

$$(I_{1.3}/8) = \text{rel. \# 1,9-decadiene units} \quad \text{Eqn. (2-2)}$$

where $I_{1.3}$ = Integral at 1.3 ppm and $I_{2.1}$ = Integral at 2.1 ppm

Using this analysis, the ratio of monomers incorporated into the polymers were compared to the monomer feed ratios (Table 2-3).

The strong correlation between the ratio of monomers in the feed with the ratio of monomers incorporated into the copolymers demonstrates that the monomer feed ratios have been maintained throughout these polymerizations. This observation is a testament to the experimental design which allowed the efficient removal of ethylene without affecting the monomer feed ratio, even though the monomers have significantly different vapor pressures.^{58,59}

Table 2-3. ^1H NMR Analysis of ADMET Copolymers Comparing the Monomer Feed Ratios with the Copolymer Composition.				
Polymer	Monomer Feed Ratio (1,9:1,5)	$I_{2.1}$	$I_{1.3}$	Ratio in Polymer (1,9:1,5)
<u>17</u>	50:50	0.40	0.41	48:52
<u>18</u>	75:25	0.31	0.45	72:28
<u>19</u>	95: 5	0.29	0.56	95: 5
<u>20</u>	25:75	0.49	0.26	26:74
$I_{2.1}$ = the integral at 2.1 ppm; and $I_{1.3}$ = the integral at 1.3 ppm 1,9 = 1,9-decadiene; and 1,5= 1,5-hexadiene				

Investigation of the Configuration of the ADMET Copolymers of 1,5-Hexadiene and 1,9-Decadiene

Quantitative ^{13}C NMR proved to be the best method for describing the microstructure of the copolymers 17, 18, 19 and 20.⁸⁸ This fact is illustrated by comparison of the ^{13}C NMR spectra of each copolymer with that of the homopolymers, while focusing on

the alkene region (129 -131 ppm). Because of the symmetric structure of the alkene bonds of the two homopolymers, polyoctenamer 6 and 1,4-polybutadiene 4, each of their spectra contains only 2 sp^2 carbon signals (one each for the cis and trans isomers). The ^{13}C NMR spectrum of polyoctenamer has an sp^2 signal at 130.3 ppm (trans) and a signal at 129.9 ppm (cis), while 1,4-polybutadiene possesses a signal at 130.0 ppm (trans), and a signal at 129.4 ppm (cis).^{89,90}

In contrast, the ^{13}C NMR spectra of the series of copolymers 17, 18, 19 and 20, exhibit eight signals each in the alkene region (Figure 2-4).⁸² Considering all possible structures for the copolymers, eight olefinic carbon signals are expected with two carbon signals each from the homopolymer linkages, accounting for four of the eight sp^2 carbon resonances. The other four carbon signals are from the unsymmetric bond formed between a 1,9-

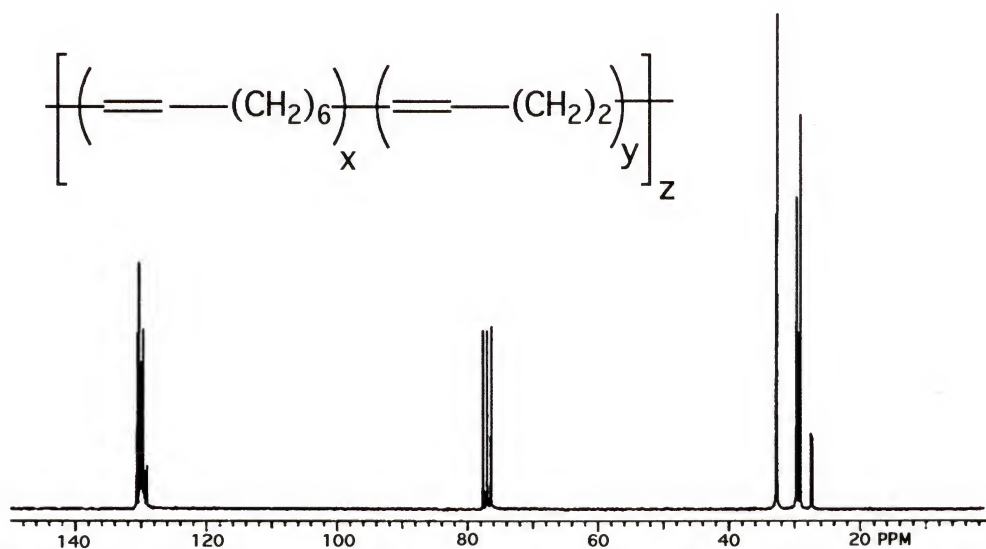


Figure 2-4. Quantitative ^{13}C NMR of the 50:50 monomer feed copolymer 17.

decadiene monomer 5 and a 1,5-hexadiene monomer 3. This bond is termed the copolymer linkage, and two distinct carbon signals are produced for the trans isomer and two more for the cis copolymer linkage.

Unequivocal assignment of each sp^2 carbon resonance in the copolymer spectra has been accomplished through the use of quantitative ^{13}C NMR.⁸⁸ The four homopolymer signals were assigned based solely upon their chemical shifts, while the copolymer linkage assignments were deduced by compilation of all of the data available. Since the sp^2 carbon signals for polyoctenamer are further downfield than the same signals in 1,4-polybutadiene, the 1,9-decadiene monomer resonances were assigned to the copolymer signals located further downfield in the ^{13}C NMR spectrum. Furthermore, the difference in chemical shift between the cis and trans isomers in the homopolymers was 0.44 ppm, with

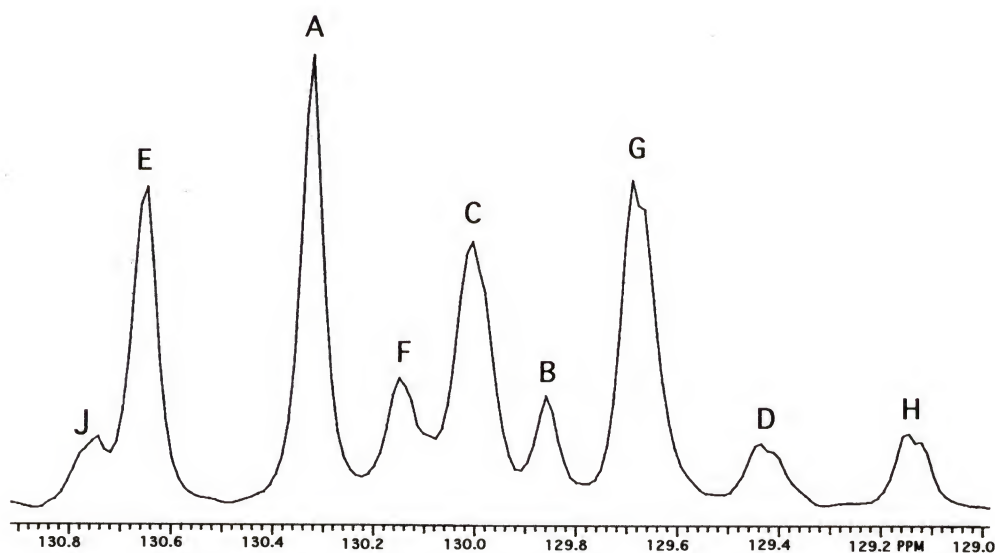


Figure 2-5. Expanded ^{13}C NMR of 50:50 copolymer 17 with peak assignment labels defined in Table (2-4).

the trans signal appearing further downfield than the cis. This difference in chemical shift between the cis and trans isomers was expected to be consistent from the homopolymer to the copolymer linkages, and aided in the assignment of the copolymer sp^2 carbon resonances. Additionally, the relative quantities of each signal had to follow a set of predetermined rules. Since the copolymer linkage was between two different monomers and resulted in two different signals for the same olefin, the resonance for the 1,9-decadiene copolymer linkage must integrate equal to the 1,5-hexadiene copolymer linkage. To the same extent, the isomeric resonances of each of these copolymer linkages must also be equal in intensity; the cis 1,9-decadiene copolymer linkage must equal the cis 1,5-hexadiene copolymer linkage, and likewise for the trans isomer.

Table 2-4. ^{13}C NMR Peak Assignments for Copolymers <u>17,18,19,20</u> . Spectrum in Figure (2-5).		
Description ^a	Chemical Shift (ppm)	Label
trans- <u>1,9</u> -1,9	131.3	A
cis- <u>1,9</u> -1,9	129.9	B
trans- <u>1,5</u> -1,5	130.0	C
cis- <u>1,5</u> -1,5	129.4	D
trans- <u>1,9</u> -1,5	130.6	E
cis- <u>1,9</u> -1,5	130.2	F
trans- <u>1,5</u> -1,9	129.7	G
cis- <u>1,5</u> -1,9	129.1	H
a) Assignment applies to the monomer of the underlined description where 1,5= 1,5-hexadiene and 1,9= 1,9-decadiene		

Utilizing all of this information, the peak assignments were successfully designated (Figure 2-5). The sp^2 carbon resonance located at 130.8 ppm, labeled J, seems to be associated with the endgroup of the copolymer since the relative intensity of this unassigned peak increases as the molecular weight of the copolymer decreases. Extrapolating from its chemical shift, the carbon associated with signal 'J' is most likely the sp^2 carbon of the internal olefin of a 1,9-decadiene monomer unit that makes up the end of a polymer chain.

Statistical Analysis of Copolymer Structure

The assignment of the carbon resonances for the copolymers, meant that statistical analysis of the microstructure of copolymers 17, 18, 19 and 20 was possible. This analysis verified the expected random sequence distribution. The mono-ads (monomer units in the copolymer) for these copolymers, already determined from 1H NMR, could also be determined from the methylene carbon resonances (26-34 ppm) (Figure 2-4).^{89,91} The carbon signal at 32.6 ppm corresponds to the two allyl methylene carbons of the trans isomer, which is present in both monomer units. The two allylic methylene carbons for the cis isomer, also present in both monomer units, are located at 27.2 ppm. The methylene carbons not adjacent to any olefin are located at 29.0, 29.2, 29.6, and 29.8 ppm; these resonances are due to the four methylene carbons present in the 1,9-decadiene monomer unit alone. Integration of the quantitative ^{13}C NMR spectra applied to the following equations, (2-3) and (2-4),

allowed for the calculation of the monomer ratios in the copolymers 17, 18, 19 and 20.

$$\frac{[(I_{32.6} + I_{27.2}) / 2] - [(I_{29.0} + I_{29.2} + I_{29.6} + I_{29.8}) / 4]}{\text{rel. \# of 1,5-hexadiene units}} = \text{Eqn. (2-3)}$$

$$\frac{[(I_{29.0} + I_{29.2} + I_{29.6} + I_{29.8}) / 4]}{\text{rel. \# of 1,9-decadiene units}} = \text{Eqn. (2-4)}$$

where I_x = the integral of the signal at 'x' ppm in the quantitative ^{13}C NMR.

Statistical analysis of the microstructure of copolymers 17, 18, 19 and 20, relied on the ability to measure the dyad sequences.⁹² The dyads have already been discussed in terms of linkages, where the homopolymer linkages are the dyads of the monomers with themselves (1,9-1,9 and 1,5-1,5), while the copolymer linkages are the dyads of the two different monomers (1,9-1,5 and 1,5-1,9).

In terms of probabilities, the mono-ad and dyad sequences are represented by the following equations:⁹²

$$P(1,9) = N(1,9)/N_t \quad \text{Eqn. (2-5)}$$

$$P(1,5) = N(1,5)/N_t \quad \text{Eqn. (2-6)}$$

$$P(1,9-1,9) = N(1,9-1,9)/N_t \quad \text{Eqn. (2-7)}$$

$$P(1,5-1,5) = N(1,5-1,5)/N_t \quad \text{Eqn. (2-8)}$$

$$\bar{P}(1,5-1,9) = [N(1,5-1,9) + N(1,9-1,5)]/N_t \quad \text{Eqn. (2-9)}$$

where, $P(A)$ represents the probability of finding monomer 'A' in the polymer chain, and $N(A)$ represents the actual number (integral) of monomers 'A' in the polymer and N_t represents the total number (integral) of monomer units present. $P(A-B)$ represents the

probability of finding the dyad where monomer 'A' is attached to monomer 'B' in the polymer, and since the direction of the dyads are indistinguishable (at least by NMR) the probability of the copolymer linkage, $\bar{P}(A-B)$ is represented as the sum of the two directionally oriented integrals, $N(A-B)$ and $N(B-A)$. The abbreviations that directly apply to the copolymers 17, 18, 19 and 20 are 1,9 = 1,9-decadiene units and 1,5 = 1,5-hexadiene units.

The mono-ad and dyad sequences are used to calculate X, the sequence order parameter, according to equation (2-10).⁹²

$$X = \bar{P}(1,5-1,9)/2 P(1,5) P(1,9) \quad \text{Eqn. (2-10)}$$

Table 2-5. Sequence Distribution Calculations.					
Polymer	Monomer Feed Ratio (1,9:1,5)	P(1,5)	P(1,9)	$\bar{P}(1,5:1,9)$	X
<u>17</u>	50:50	0.49	0.51	0.59	1.2
<u>18</u>	75:25	0.78	0.22	0.46	1.2
<u>19</u>	95: 5	0.92	0.08	0.17	1.1
<u>20</u>	25:75	0.24	0.76	0.39	1.1
<u>21</u>	sequential	0.48	0.52	0.42	0.83
<u>22</u>	sequential	0.48	0.52	0.29	0.59

A value of $X = 1.0$ indicates that the monomer units are random or statistically distributed throughout the copolymer, while a value of $X = 0.0$ indicates that the polymer is a block copolymer.⁹² The values of X reported here confirm that all of the copolymers

produced from the pre-mixed monomer feeds are random in distribution. Since this was the expected result, these findings support the ^{13}C NMR peak assignments made for these previously unknown copolymers.

Copolymer Synthesis Through Transmetathesis with Existing Homopolymers

It is worth noting that existing polymers can be modified through the transmetathesis reaction (Figure 2-6). The homopolymer, polyoctenamer 6, was modified by the addition of an equimolar amount of 1,5-hexadiene 3, producing copolymer 17a, which was random in nature with a X value of 1.13. The same

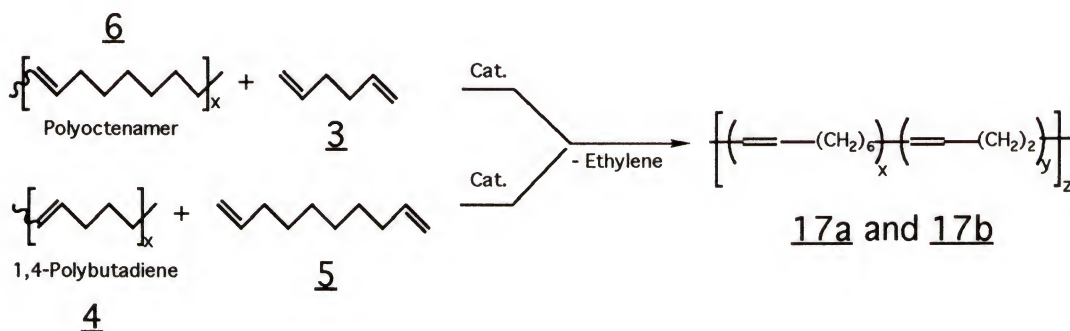


Figure 2-6. The synthesis of random copolymers by the transmetathesis of existing homopolymers and monomer.

polymer was synthesized starting with the homopolymer, 1,4-polybutadiene 4, and adding an equimolar amount of 1,9-decadiene 5, termed copolymer 17b, and was indistinguishable from the other 50:50 copolymers, 17 and 17a. This result means that any ADMET polymer, or any polymer containing unsaturated bonds, can be

chemically modified into a random copolymer of predictable composition, provided it is compatible with ADMET chemistry.

Block Copolymer Synthesis

All of the above copolymerizations were performed with catalyst 15, $W(CHCMe_2C_6H_5)(N-2,6-C_6H_3-iPr_2)[OCCH_3CF_3]_2]_2$, which is reported to be more reactive towards internal olefins than vinyl groups. However, catalyst 16, $Mo(CHCMe_2C_5H_6)(N-2,6-C_6H_3-iPr_2)[OCCH_3CF_3]_2]_2$, has been reported to be more reactive towards vinyl units than internal olefins.⁹³ Additionally, catalyst 16 has been shown to be significantly faster in polymerizing 1,9-decadiene.⁶⁸ The selectivity of catalyst 16 coupled with the faster reaction kinetics offered an opportunity to synthesize block copolymers with ADMET polymerization techniques.

In living polymerizations, sequential monomer addition leads to block copolymer formation, but ADMET chemistry has been demonstrated to be a step condensation polymerization where the catalyst is not always attached to the growing polymer chain. An artifact of the step condensation mechanism is the randomized distribution of monomers in a copolymer through the transmetathesis reaction (Figure 2-1).⁸³ However, since ADMET polymerizations are performed in the absence of solvent, sequential addition of monomers offered the opportunity to synthesize block copolymers with ADMET polymerization techniques. By homopolymerizing the first monomer, producing a solid, the concentration of the internal olefin would be essentially zero when the second monomer was added. By polymerizing the second

monomer before the homopolymer of the first monomer dissolved the degree of transmetathesis between these two reactive species could be significantly lowered.

The first experiment aimed at forming block copolymers via ADMET techniques employed the same two monomers, 1,9-decadiene 5 and 1,5-hexadiene 3, and the molybdenum based catalyst 16. 1,9-Decadiene 5 was homopolymerized, followed by the condensation of an equimolar amount of 1,5-hexadiene 3 into the reaction flask. The act of cooling the reaction in liquid nitrogen destroyed the catalytic activity of this sensitive catalyst 16, thus dictating a second addition of catalyst 16. The process of introducing additional catalyst provided sufficient time for the polyoctenamer to dissolve in the monomer 3, thus creating the reaction conditions that favor the transmetathesis reaction, and the resulting block content of the copolymer 21 was lower than anticipated. However, the results of

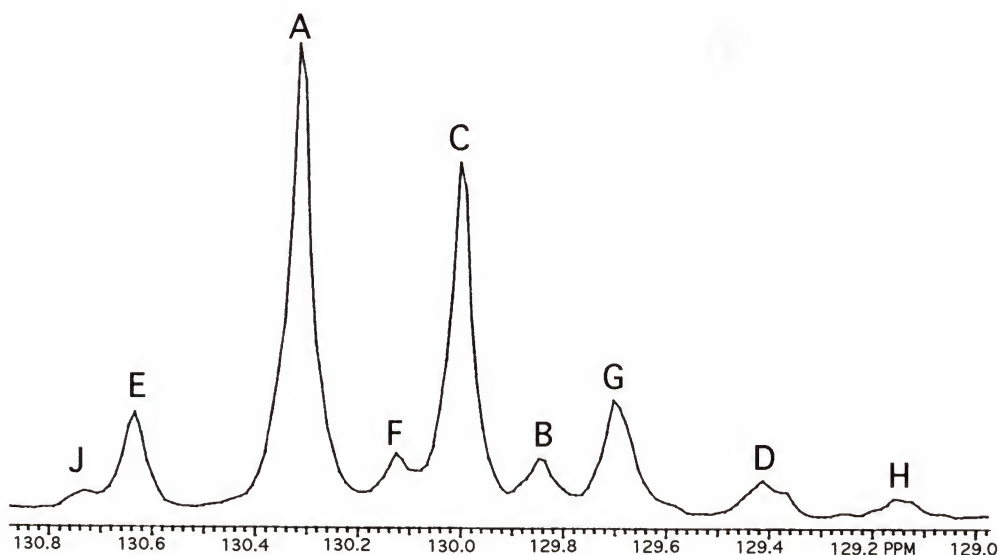


Figure 2-7. Expanded quantitative ^{13}C NMR of 'block' copolymer 22.

this experiment were encouraging since the homopolymer content of this copolymer 21 was increased over the random copolymer as illustrated by the lower X value (Table 2-6). It was apparent that the second monomer addition had to be accomplished without destroying the catalyst.

The sequential addition of monomers was repeated, but this time, the second monomer, 1,5-hexadiene 3, was syringed onto to the solid polyoctenamer under an inert atmosphere. The copolymer produced from this reaction, polymer 22, was much more block-like in structure, with a calculated X value of 0.585 (Table 2-6). The homopolymer linkages in the ^{13}C NMR of copolymer 22 are more abundant when compared to that of the random copolymer 17 (Figure 2-7) while the presence of the copolymer linkages 'E', 'F', 'G', and 'H', rules out the argument that copolymer 22 is only a mixture of homopolymers.

Table 2-6. Average Sequence Length Calculations.						
Polymer	P(1,5-1,5)	P(1,9-1,9)	$\bar{P}(1,5-1,9)$	X	$l_{1,5}$	$l_{1,9}$
<u>17</u>	0.24	0.26	0.59	1.2	1.8	1.9
<u>21</u>	0.23	0.26	0.52	0.83	3.8	4.0
<u>22</u>	0.36	0.35	0.29	0.59	6.9	6.8

As an indicator for the relative success of the synthesis of block copolymers by the ADMET reaction, the average sequence length, l_A , was calculated from the dyad sequences (Eqn. 2-11).⁹²

$$l_A = [P(AA) + 0.5 \bar{P}(AB)] / 0.5 \bar{P}(AB) \quad \text{Eqn. (2-11)}$$

This statistic indicates the average number of consecutive monomer units present in the copolymer chain, and has been calculated for the 'block' copolymers synthesized, 21 and 22, as well as the random copolymer 17 for comparison purposes (Table 2-6).

The first attempt at block copolymer formation via ADMET chemistry was somewhat successful as evidenced by the more than two fold increase in the average sequence length of polymer 21 relative to the random copolymer. The second attempt at block copolymer formation via ADMET chemistry showed an even larger decrease in the value of X to 0.59 for polymer 22, indicating the larger deviation from the random distribution of monomers. The number average sequence length of copolymer 22 was increased to a value approaching 7.0, more than a three fold increase over the random copolymer value of 1.89. Although ADMET chemistry is not ideally suited for the synthesis of true block copolymers, at least in the case for monomers of similar reactivity, it has been demonstrated that by careful manipulation of the reaction conditions some degree of control over the copolymer microstructure is possible.

More importantly, the results presented in this chapter have demonstrated that ADMET polymerization techniques are effective in the production of copolymers when a mixed comonomer feed is utilized. Through the application of known statistical analysis methods, the microstructure of copolymers 17, 18, 19, and 20 has been established as a random sequence distribution, which is an artifact of the step condensation mechanism of ADMET polymerizations. Additionally, existing homopolymers have been

shown to undergo transmetathesis to produce random copolymers. With these results comes the knowledge that the syntheses of a variety of copolymers are possible; in fact, since the completion of this work a number of copolymers have been synthesized with ADMET polymerization techniques, among these copolymers is a series of alternating copolymers that will be discussed later in this dissertation.

CHAPTER 3

THE METATHESIS ACTIVITY OF 1,1-DISUBSTITUTED AND TRISUBSTITUTED OLEFINS

With the copolymerization of 1,5-hexadiene 3 and 1,9-decadiene 5, acyclic diene metathesis (ADMET) polymerization chemistry was extended beyond the synthesis of previously known polymers, but the scope of this relatively new step condensation polymerization reaction needed to be broadened further, beyond the synthesis of linear hydrocarbon polymers.⁸² Great strides have been made with respect to the incorporation of various functionalities in the ADMET polymerization scheme; specifically, monomers containing ethers,⁷¹ thioethers,⁷² silanes,⁹⁴ siloxanes,^{79,80} ketones,⁷³ esters,⁷⁵ carbonates,⁷⁷ and conjugated pi systems⁹⁵ have all been polymerized. Whereas the electronic effects of some

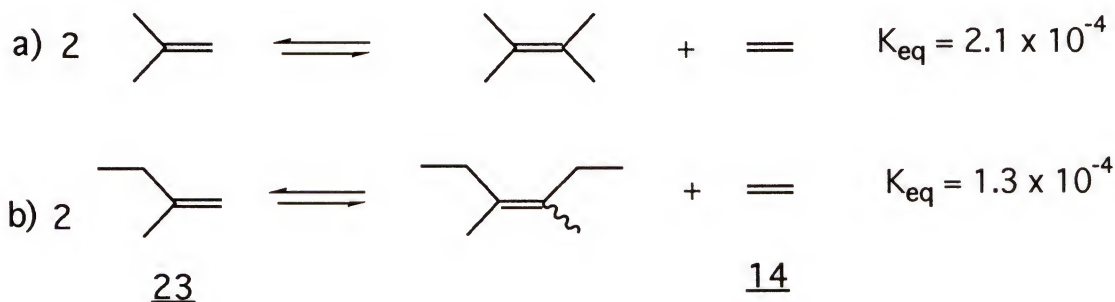


Figure 3-1. Disproportionation of isobutene and 2-methylbutene demonstrating and the thermodynamic equilibrium values calculated from data in Rosini.^{66,67}

of these groups on ADMET polymerization chemistry have been elucidated, the steric effects of branching along the monomer backbone had not been investigated.

Thermodynamic data shows that the disproportionation of 1,1-disubstituted olefins is energetically unfavorable. Isobutene at 25 °C has an equilibrium distribution of 1.4 % for each of the products, while the equilibrium values for the higher analogues are even lower.⁶⁶ Despite such a small equilibrium value, the disproportionation of 2-methylbutene 23 has been driven to 95% completion by the removal of ethylene 14 (Figure 3-1).⁹⁶

Additional examples of the metathesis of 1,1-disubstituted olefins are available; however, all utilize a classical Lewis acid catalyst system, and such catalysis systems interfere with ADMET polymerizations via competing side reactions such as vinyl addition chemistry.⁵⁷ The goal of the research reported herein has been to study the effects of 1,1-disubstitution of the functional alkene on the olefin metathesis reaction as it pertains to ADMET polymerization; thus the catalysts employed for this investigation were the Lewis acid free alkylidenes, 15 and 16, which successfully polymerize acyclic dienes.

Attempted Metathesis of 1,1-Disubstituted Dienes

The reported successful formation of tetrasubstituted olefins with classical metathesis catalyst systems prompted the investigation of the potential application of 1,1-disubstituted alkenes to ADMET polymerizations.⁹⁷ The potential monomer, 2,5-

dimethyl-1,5-hexadiene 24, was used to investigate the effect of direct substitution of the olefin functionality on the metathesis activity employing ADMET techniques. This compound was of particular interest since successful metathesis would produce a polymer best described as a methyl substituted polyisoprene (Figure 3-2). Both catalysts 15 and 16 failed to produce the tetrasubstituted olefin, as pure 24 was isolated from each attempted metathesis reaction.

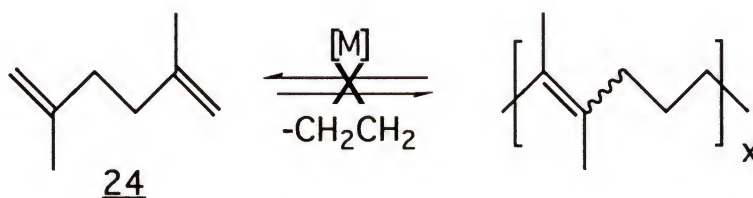
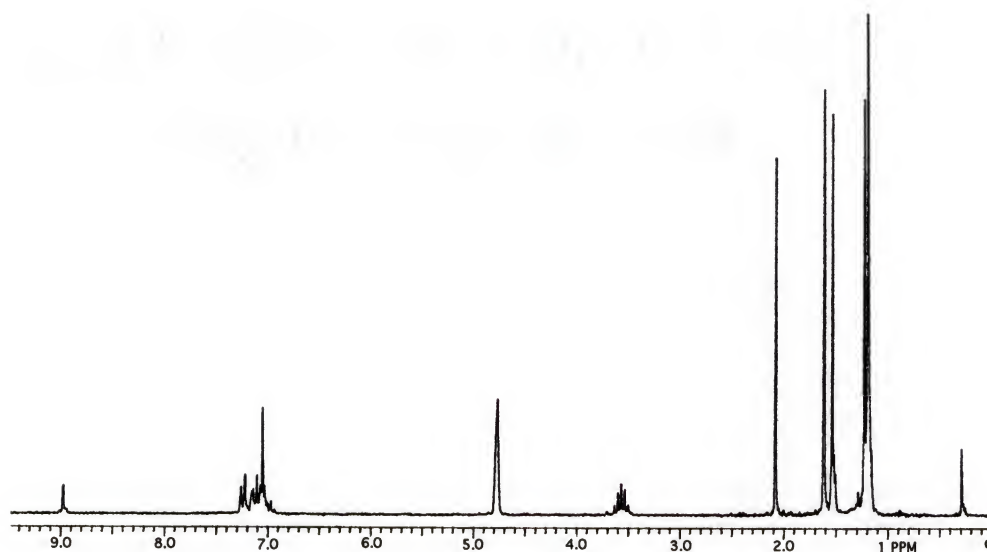
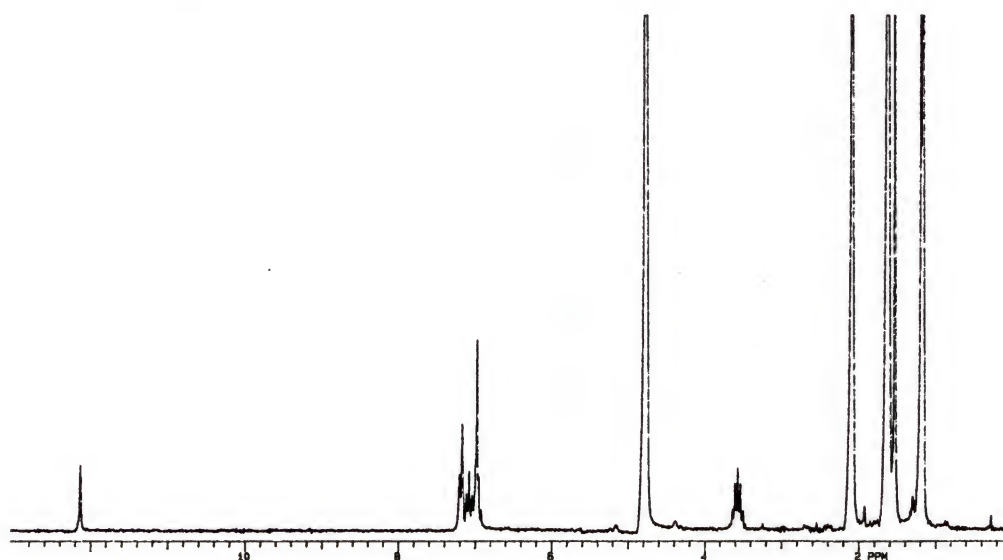


Figure 3-2. Potential polymerization of 2,5-dimethyl-1,5-hexadiene 24, where [M] represents catalysts 15 or 16.

Monitoring the interaction of 24 with each catalyst by ^1H NMR provided further insight into the metathesis activity of this substituted diene, as well as confirming the above results. Not only was no productive metathesis observed, but there was no observed interaction between the diene and the initial alkylidene of either catalyst. The solution of 24 with the tungsten catalyst 15 showed the alkylidene proton (9.0 ppm) unchanged from that of the pure



a) ^1H NMR spectrum of 2,5-dimethyl-1,5-hexadiene 24 in the presence of the tungsten catalyst 15.



b) ^1H NMR spectrum of 2,5-dimethyl-1,5-hexadiene 24 in the presence of the molybdenum catalyst 16.

Figure 3-3. ^1H NMR spectral analysis of 2,5-dimethyl-1,5-hexadiene 24 with catalysts 15 and 16.

catalyst,⁸⁴ while the methylene protons of the olefin of 24 (4.8 ppm) also remain unchanged (Figure 3-3a). Although the formation of the internal olefin would not produce a proton signal for this bond, the methyl group (1.2 ppm) would be expected to exhibit a significant shift in its position, while the proton signal accompanying the production of ethylene (necessary for the productive metathesis reaction) would also be detectable (5.3 ppm).⁹⁸ Neither of these changes was observed, suggesting that no reaction had taken place. Analogously, the solution of 2,5-dimethyl-1,5-hexadiene 24 with the molybdenum catalyst 16 exhibited the original alkylidene proton signal at 12.2 ppm,⁹³ and the unreacted diene resonances, without the detection of an ethylene signal (Figure 3-3b).

Any reaction of the initial alkylidene would have resulted in the release of the 3-methyl-3-phenylbutene 26 according to Figure (3-4) accompanied by the relative decrease in the original alkylidene proton signal. Neither of these spectra showed any changes as the solutions were incubated at 50 °C for 72 hr, attesting to the inert nature of 2,5-dimethyl-1,5-hexadiene 24 with both catalysts.

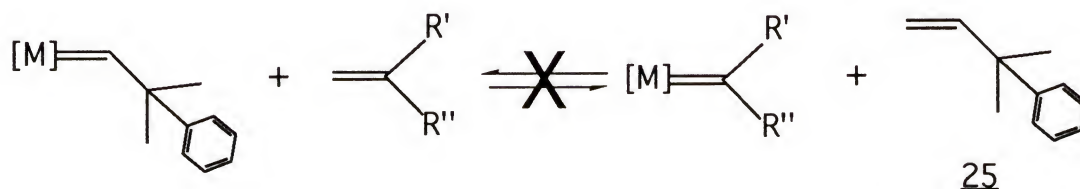


Figure 3-4. The nonproductive metathesis of the initial alkylidene to release 3-methyl-3-phenylbutene 26, where [M] represents catalysts 15 and 16.

The results presented above indicate that alkenes containing a methyl group on the internal olefinic carbon are excluded from all reactions with the catalysts 15 and 16. This constraint may be limited to the interaction of the initial alkylidene with the reactant, which is discussed further in the next section.

Metathesis of an Unsymmetrically Substituted Diene with the Tungsten Catalyst

The metathesis 'catalyst' added to these reactions is actually a pre-catalyst, since the actual catalytic species is generated in situ by the non-productive metathesis reaction of the initial alkylidene with the alkene reactant (Figure 3-4). In fact, proton NMR analysis showed that the actual catalytic species never was generated in the presence of 2,5-dimethyl-1,5-hexadiene 24. The interaction of the initial alkylidene with the methyl substituted vinyl group might have prevented the formation of the catalytic alkylidene; in order to draw any conclusions about the reactivity of the 1,1-disubstituted vinyl group, the catalytic alkylidene was generated in the presence of the alpha substituted olefin. For this purpose, 2-methyl-1,5-hexadiene 27 was exposed to the tungsten catalyst 15 under ADMET reaction conditions (Figure 3-5).

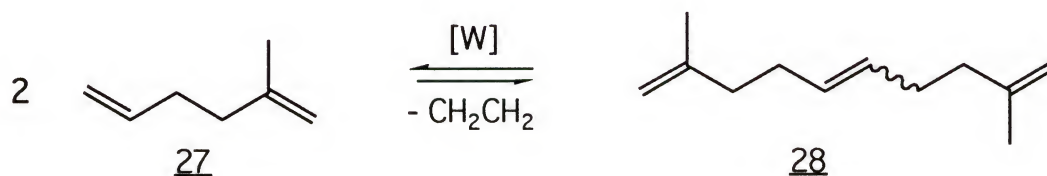
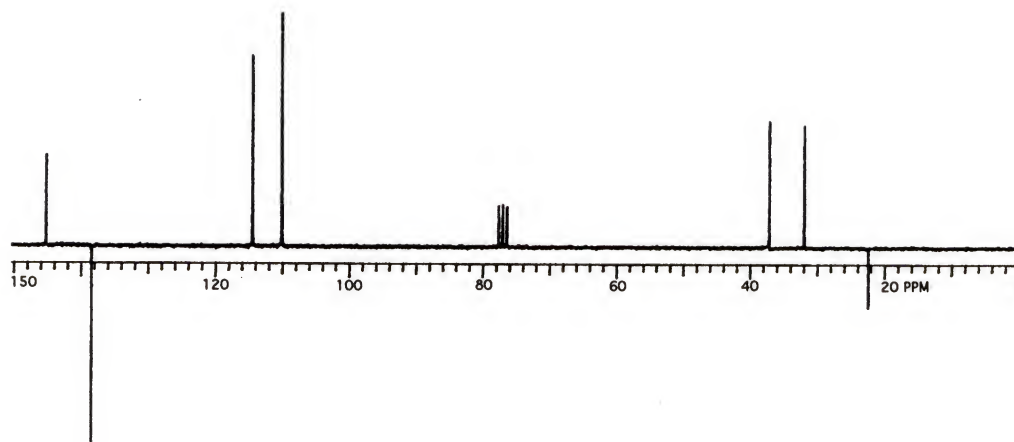
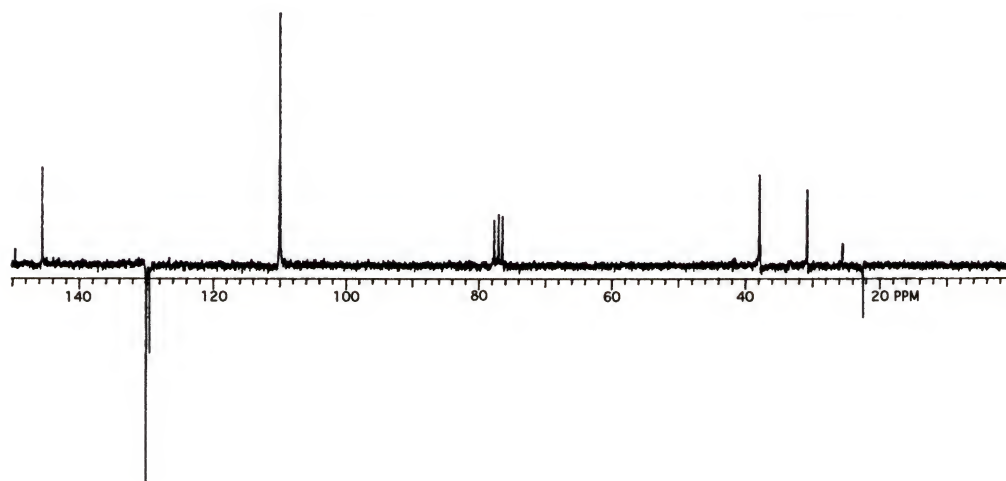


Figure 3-5. Dimerization of 2-methyl-1,5-hexadiene 27 where [W] represents the tungsten catalyst 15.



a) APT ^{13}C NMR spectrum of 2-methyl-1,5-hexadiene 27.



b) APT ^{13}C NMR spectrum of 2,9-dimethyl-1,5,9-decatriene 28.

Figure 3-6. ^{13}C NMR analysis of the dimerization of 2-methyl-1,5-hexadiene 27 with the tungsten catalyst 15.

The ^{13}C NMR spectrum of the reaction solution shows that in addition to ethylene, the dimer, 2,9-dimethyl-1,5,9-decatriene 28, produced from the exclusive metathesis of the unsubstituted olefin, was the only product (Figure 3-6). The alkene region (110-150 ppm) of the ^{13}C NMR spectrum of 27 has four carbon signals, one for each sp^2 carbon of the two different olefins: (CH_2 , 110.0 ppm),

(quaternary carbon 145.4 ppm), (CH, 112.4 ppm), and (CH₂, vinyl, 138.4 ppm). The vinyl carbons are absent in the spectrum of the reaction product 28, but the 1,1-disubstituted carbon signals remain. Only the unsubstituted vinyl group metathesized to form the internal (CH) olefin represented by the cis/trans carbon signals (129.8 ppm, 130.0 ppm), while the methylene carbons were removed from the reaction as ethylene.

There is no doubt that the catalytic species, methyldiene 25a, had been generated during the course of this dimerization reaction, and yet the 1,1-disubstituted olefin did not metathesize. However, the total lack of participation of the 1,1-disubstituted alkene unit of 27 in the metathesis reaction does not prove that this olefin is incapable of undergoing productive metathesis with catalyst 15 since competition between the two different olefins cannot be dismissed. The only conclusion that can be drawn from this reaction is that the vinyl group possesses a much greater reactivity than the 1,1-disubstituted olefin.

Generation of the actual catalytic species, methyldiene 25a, of catalyst 15 in the presence of 2,5-dimethyl-1,5-hexadiene 24 was the only true test of metathetic activity. Since

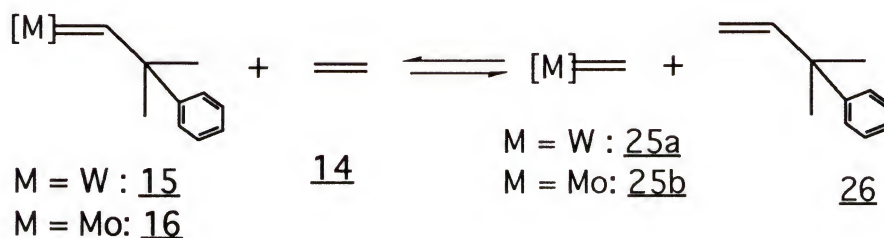


Figure 3-7. The generation of the methyldiene by the reaction of ethylene with the neophylidene where [M] represents catalysts 15 or 16.

ethylene is known to react with the initial alkylidene 15 to produce the methylidene 25a,⁸⁴ ethylene was introduced into a reaction vessel containing catalyst 15 and 1,5-hexadiene 24, allowed to react for two hours, and subsequently removed. Thus the reactivity of the 1,1-disubstituted olefin was addressed with the true metathesis catalyst, without the issue of olefin competition. No evidence of productive metathesis was observed, meaning that the 1,1-disubstituted alkene of 24 is inert to the tungsten catalyst 15, in both the pre-catalytic and catalytic forms. Therefore, steric hinderence dictates the products attainable with this catalyst system.

Polymerization of an Unsymmetrically Substituted Diene with the Molybdenum Catalyst

The metathesis of 2-methyl-1,5-hexadiene 27 with the molybdenum catalyst 16, proved to be much more successful than for the tungsten version. In fact, the incipient reaction was quite violent, with the rapid generation of ethylene causing the solution to foam. ¹³C NMR revealed that the monomer initially dimerized to 2,9-dimethyl-1,5,9-decatriene 28 solely by the metathesis of the unsubstituted vinyl group. The reaction proceeded slowly as the substituted vinyl groups underwent transmetathesis with the internal olefins to produce a polymer, the structure of which is essentially identical to that of 1,4-polyisoprene (Figure 3-8). Therefore the molybdenum catalyst is capable of overcoming the steric constraints that inhibited the tungsten catalyst 15 in

metathesizing 1,1-disubstituted alkenes. This significant difference in catalytic activity is discussed in more detail in later sections.

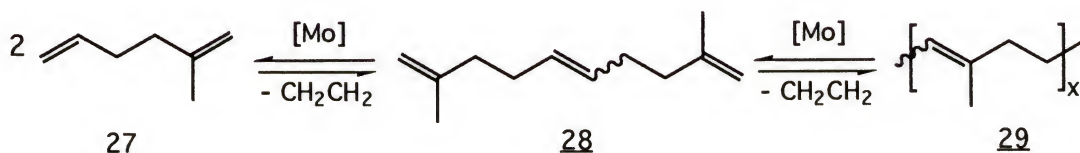


Figure 3-8. Reaction of 2-methyl-1,5-hexadiene **27** with catalyst **16** illustrating the relative reactivity of each olefin.

NMR Analysis of 1,4-Polyisoprene Synthesized by the ADMET Polymerization of 2-Methyl-1,5-hexadiene

Traditionally, 1,4-polyisoprene is synthesized by the anionic polymerization of 2-methyl-1,3-butadiene (isoprene) through a 1,4 addition reaction.⁹⁹ Depending on the reaction conditions, especially the combination of solvent, temperature and gegen ion employed, the anionic polymerization of isoprene results in a variable amount of 1,4; 1,3 and 1,2 addition products in the polymer backbone.⁹⁹

The spectral analysis of polymer **29** is consistent with the spectra of anionically synthesized 1,4-polyisoprene.¹⁰⁰ The ^1H NMR of this new ADMET polymer **29** exhibits the internal olefin signal (5.1 ppm), while a small amount of unreacted vinyl protons are also detected, 4.7 and 5.4 ppm (Figure 3-9). The two different methylene proton signals overlap at 2.0 ppm producing a broad signal with a shoulder. The relative contributions of the E and Z isomers are revealed by the two separate proton signals at 1.7 ppm (E) and 1.6 ppm (Z), while the Z/E ratio for polymer **29** calculated from the integration of these resonances is 0.54.

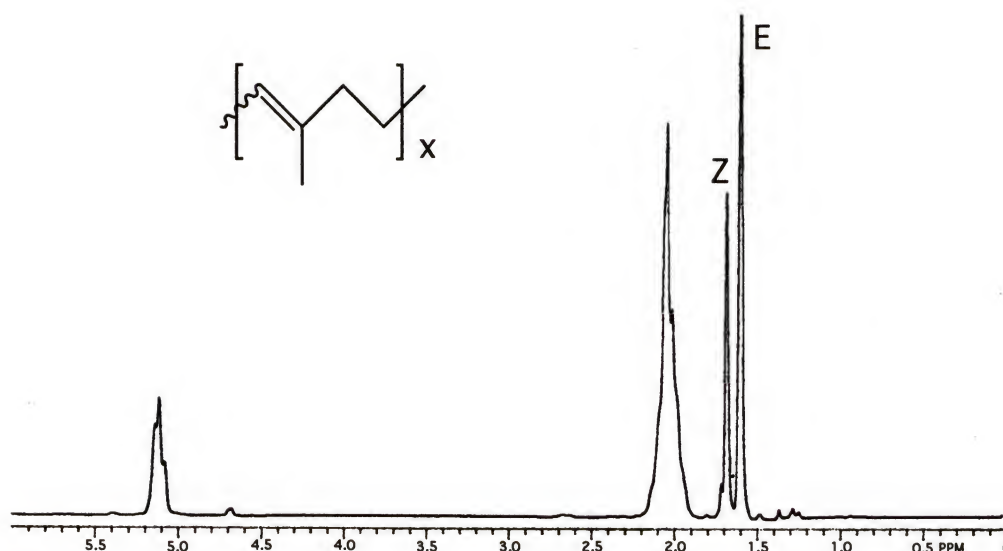


Figure 3-9. ^1H NMR spectrum of polyisoprene produced by the ADMET polymerization of 27 with catalyst 16.

The quantitative ^{13}C NMR of this new ADMET polymer 29, also essentially matches that of anionically synthesized 1,4-polyisoprene.¹⁰¹ The E/Z ratio calculated from the resonances at 125.1 ppm (Z) and 124.3 ppm (E), determined to be 0.53, is in agreement with the ^1H NMR integration. However, there are additional carbon signals present in the spectra of polymer 29 that do not correspond to 1,4-polyisoprene. Specifically, the resonance at 130.0 ppm is due to a small amount of unsubstituted internal olefin that remains from the dimer, 2,9-dimethyl-1,3,5-decatriene 28. The endgroups, which are methyl substituted vinyl groups, are also observed (110.0 ppm, 145.4 ppm). The number average molecular weight calculated from the integration of the endgroup resonances relative to the internal olefinic carbons was 6,800 g/mol. This relatively low molecular weight is most likely a result of the slow reaction kinetics of the transmetathesis reaction

involving the methyl substituted vinyl group. The molecular weight of polymer 29 most likely would increase with increased reaction time.

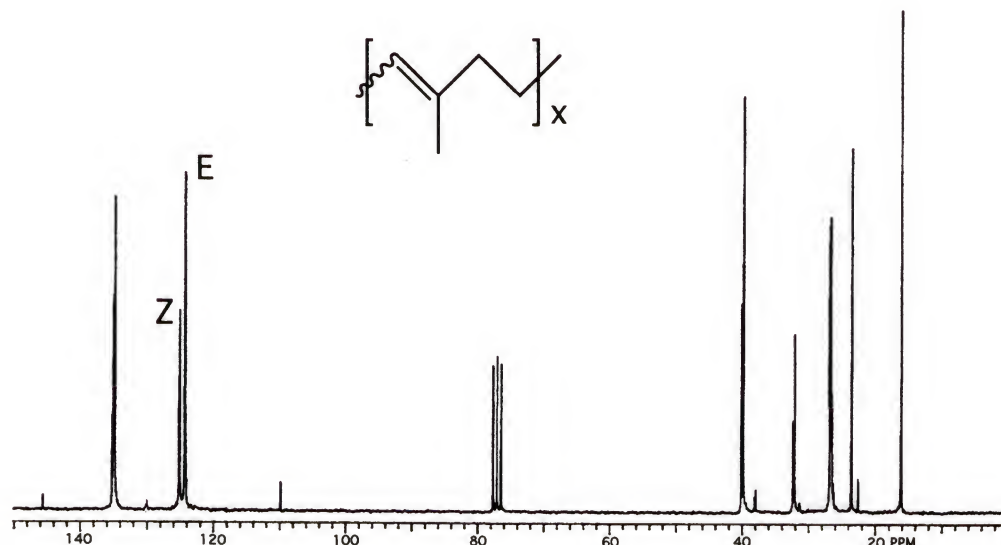


Figure 3-10. Quantitative ^{13}C NMR spectrum of polyisoprene produced by the ADMET polymerization of 27.

The olefin metathesis reaction has previously been utilized in the synthesis of 1,4-polyisoprene by the ring opening metathesis polymerization (ROMP) of 1-methylcyclobutene 30 with $\text{Ph}_2\text{C}=\text{W}(\text{CO})_5$ as catalyst and produced a polymer that consisted of 80% isoprene units, and the other 20% disubstituted and tetrasubstituted double bonds (Figure 3-11).¹⁰²



Figure 3-11. ROMP of 1-methylcyclobutene 30.¹⁰²

Totally absent from the ADMET polymer 29 was the tetrasubstituted olefin, which is consistent with the observations recently reported by Grubbs et al.^{103,104} Employing catalyst 16, these investigators reported on the cyclization of various dienes, specifically ethers, amines and amides. They found that cyclization occurred with 1,1-disubstituted olefins provided the product was trisubstituted not tetrasubstituted. In other words, one of the reacting olefins must be unsubstituted for productive metathesis to occur. This requisite is substantiated by the formation of polyisoprene free of tetrasubstituted olefinic units from the ADMET polymerization of 2-methyl-1,5-hexadiene 27.

One possible explanation for this reaction preference is a bias towards the formation of monosubstituted alkylidenes, since the presence of a methyl substituent directly on the vinyl group may prevent the participation of this functionality in alkylidene formation. It is conceivable that the 1,1-disubstituted alkene participates in productive metathesis solely as the second olefin. In

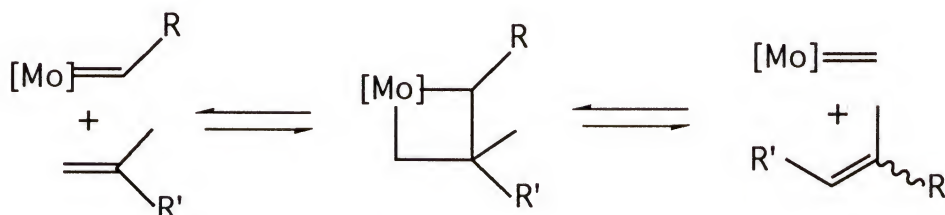


Figure 3-12. Proposed metallacycle produced in the ADMET synthesis of polyisoprene from 2-methyl-1,5-hexadiene 27, where [Mo] represents catalyst 16.

this way, the methyl substituent is only located on the beta carbon of the metallacycle (Figure 3-12). Although there is no direct evidence supporting this explanation, the failure of 2,5-dimethyl-1,5-hexadiene 24 to interact with the molybdenum catalyst 16 lends some support to this theory.

Attempted Metathesis of a Conjugated 1,1-Disubstituted Diene

While the energetics of the formation of a tetrasubstituted olefin are unfavorable, the delocalization energy associated with an increase in conjugation in the metathesis product might help drive this reaction forward. For this study, the potential monomer 1,4-diisopropenylbenzene 31 was employed (Figure 3-13). The phenyl ring would not only provide the conjugation between the dienes of the monomer, but also relieve some of the steric constraints associated with the formation of a tetrasubstituted alkene.

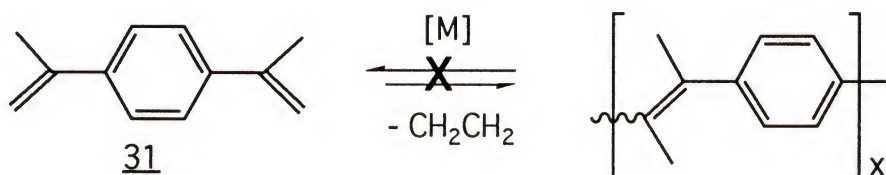


Figure 3-13. Potential metathesis reaction of 1,4-diisopropenylbenzene 31, where [M] represents catalysts 15 or 16.

Only starting materials were isolated in repeated attempts to metathesize 31 with both catalysts 15 and 16. As demonstrated by the ^1H NMR of the solution containing both 31 and the tungsten catalyst 15, 31 possesses the activity demonstrated by 2,5-

dimethyl-1,5-hexadiene 24, as it is inert to the 'pre-catalyst' (Figure 3-14).

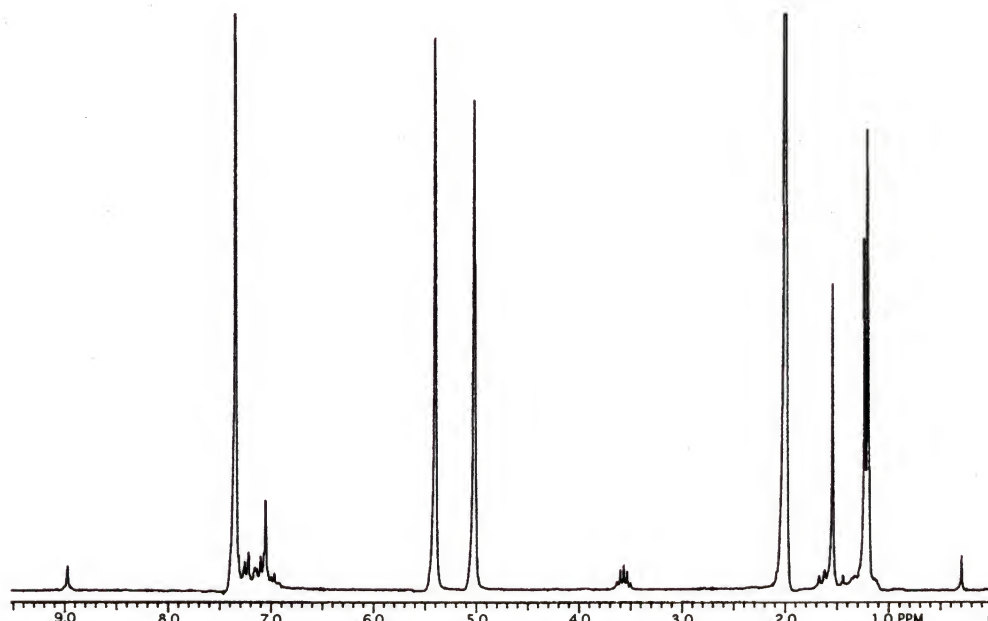


Figure 3-14. ^1H NMR spectrum of 1,4-diisopropenylbenzene 31 in the presence of the tungsten catalyst 15.

Ethylene was added to these reactions in an effort to test the metathesis activity of 31 with the methyldiene of catalysts 15 and 16, but failed to bring about any productive metathesis.

Transmetathesis of a Trisubstituted Olefin

Theoretical thermodynamic equilibrium data shows that the disproportionation of 2-methyl-2-butene 32 is more favorable than the disproportionation of isobutene (Figure 3-15). Accordingly,

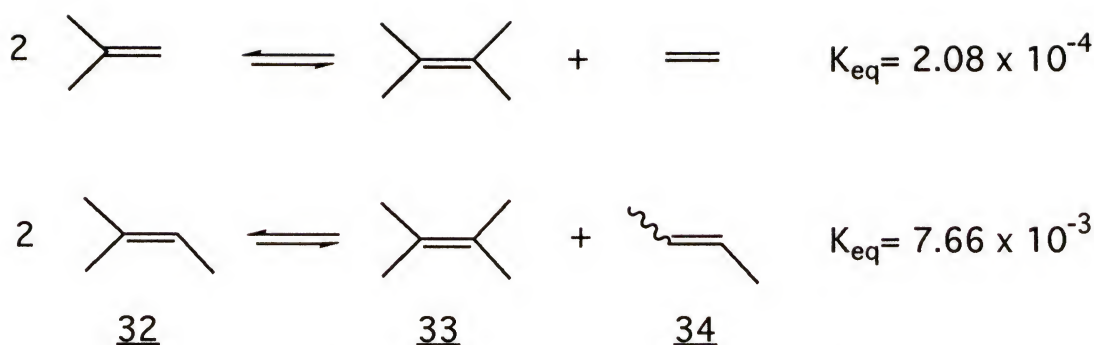


Figure 3-15. Disproportionation of 2-methyl-2-butene and isobutene and the calculated thermodynamic equilibrium values.^{66,67}

the metathesis activity of 2-methyl-2-butene 32 was studied in a closed system to test the feasibility of the formation of a tetrasubstituted alkene with the ADMET catalysts 15 and 16. Previous attempts at producing such an olefin with these catalysts failed, but the metathesis of 32 represents the first attempt employing a trisubstituted alkene, as well as the most favorably substituted alkene since the methyl groups present the smallest steric influence on the metathesis reaction.

After allowing the reaction with each catalyst to stand undisturbed for one week, the solutions were analyzed via high resolution gas chromatography coupled mass spectroscopy. Integration of the gas chromatogram of each of these solutions revealed mixtures of cis and trans 2-butene 34, 2-methyl-2-butene 32 and 2,3-dimethyl-2-butene 33 in relative concentrations that closely matched the predicted values for a thermodynamic equilibrium (Table 3-1).

Table 3-1. Equilibrium Disproportionation of 2-Methyl-2-butene.
Values are Mole Percents. see Figure (3-15)

Catalyst	2-Methyl-2-butene <u>32</u>	2,3-Dimethyl-2-butene <u>33</u>	2-Butene <u>34</u> (cis & trans)
Theoretical	85.1	7.45	7.45
<u>15</u>	83	8.7	8.3
<u>16</u>	84	7.9	7.7

This successful metathesis reaction is a rare example of the metathesis of a trisubstituted alkene.³ Since 32 represented the lowest possible steric situation for the metathesis of a trisubstituted olefin, it remained to be illustrated that such a functionality could be applied to an ADMET polymerization scheme, which requires the replacement of one of the methyl groups with an alkyl chain.

Attempted Polymerization of a Trisubstituted Diene

The ADMET polymerization of 3,6-dimethyl-2,6-octadiene 35 would produce the same polymer structure anticipated from the failed polymerization of 2,5-dimethyl-1,5-hexadiene 24, the only difference being that 2-butene would evolve rather than ethylene (Figure 3-16). The trisubstituted alkenes of 35 represent the extension of the successfully metathesized 2-methyl-2-butene 32 functionality to ADMET polymerization chemistry, where one of the methyl groups of 32 is replaced with a connecting alkyl chain.

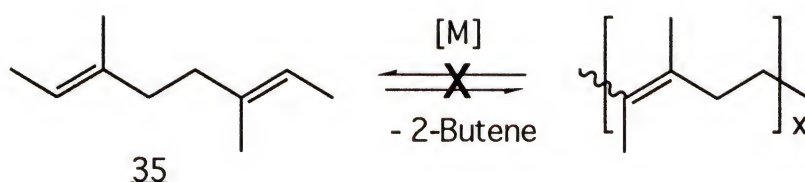


Figure 3-16. Potential polymerization reaction of 3,6-dimethyl-2,6-octadiene 35, where [M] represents catalyst 15 or 16.

The trisubstituted olefin was employed in order to take advantage of the more favorable equilibrium as compared to that of 1,1-disubstituted alkenes; however, the increased substitution had no positive effect on the metathesis reaction as 35 showed no productive metathesis with either catalyst 15 or 16. The addition of ethylene to these reactions also failed to bring about the metathesis of the trisubstituted alkenes.

The lack of any productive metathesis of 35 in the presence of catalysts 15 and 16 suggests that the size of the substituents is important. The same holds true for the absence of any tetrasubstituted olefins in the polymerization of 2-methyl-1,5-hexadiene 27 (Figure 3-8). In fact, the trimethyl substituted alkene 32 is the only trisubstituted olefin that demonstrated any productive metathesis activity. Any application to ADMET polymerization chemistry which requires the formation of a tetrasubstituted olefin appears unattainable.

Attempted Polymerization of a Trisubstituted Polyene

The structure of squalene 36 afforded the opportunity to produce 2,3-dimethyl-2-butene 33 as the condensate of an ADMET

polymerization (Figure 3-17), which is essentially the reverse of the situation for 3,6-dimethyl-2,6-octadiene, where the polymer would have contained the tetrasubstituted alkene produced. The metathesis of the endgroup alkene of squalene 36 is analogous to the transmetathesis of 3-methyl-2-butene 32 with the distinction that the alkyl backbone of 36 replaces one of the methyl groups of 3-methyl-2-butene 32. The endgroups of squalene 36 were expected to be more the reactive olefin due to the higher order of substitution on the internal alkenes. An additional advantage associated with the structure of squalene 36 was its low vapor pressure which allowed direct high vacuum to be applied to the reaction without loss of monomer.

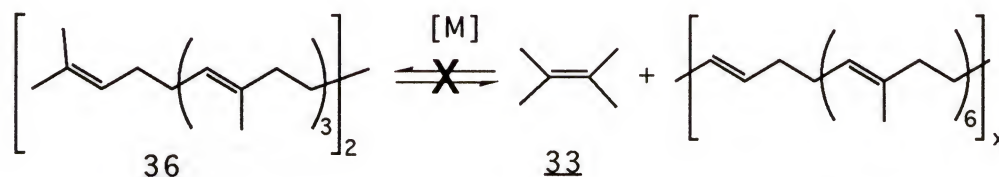


Figure 3-17. Attempted polymerization of squalene 36, where [M] represents catalyst 15 or 16.

No productive metathesis was observed for the reaction of squalene 36 with either catalyst 15 or 16, and the attempted activation of these catalysts with ethylene again proved unsuccessful. The lack of metathesis activity demonstrated by both 35 and 36 illustrates that the substitution pattern of these trisubstituted olefins is of no consequence in determining their metathesis activity with catalysts 15 and 16.

Attempted Metathesis of an 1,1-Disubstituted Exocyclic Alkene

Methylenecyclohexane 37 was employed as a model compound in an effort to relieve the steric constraints of the metathesis reaction of 1,1-disubstituted olefins. Tying back the alkyl substituents in a six membered ring, could make the alkene more accessible to the metal center of the catalyst (Figure 3-18).

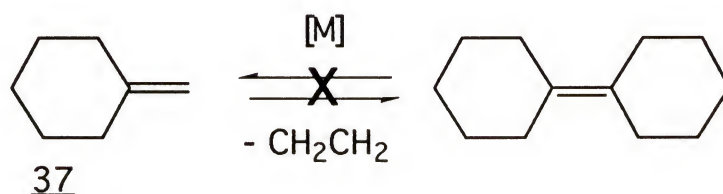
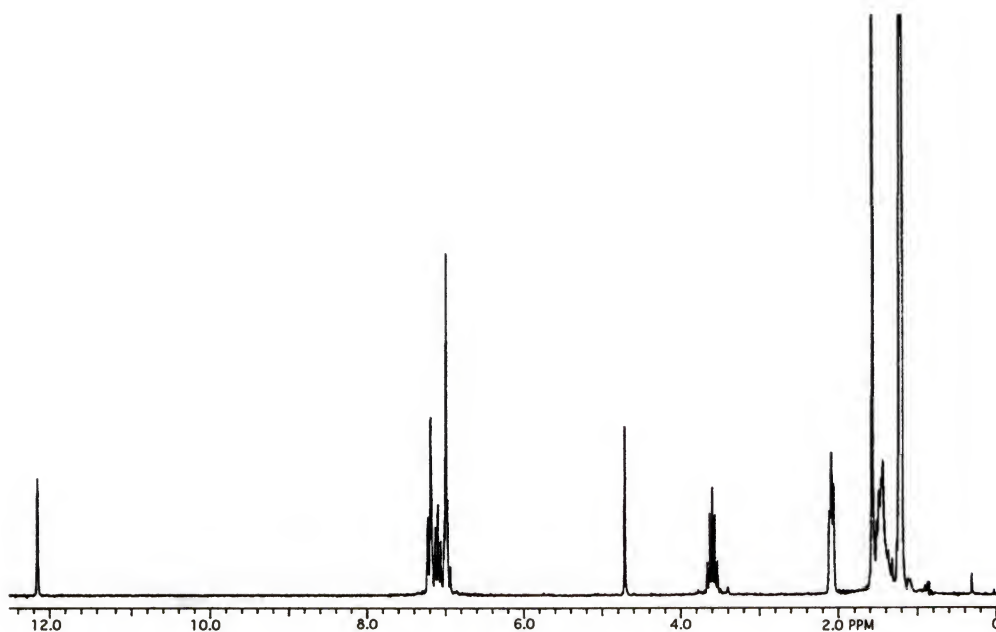
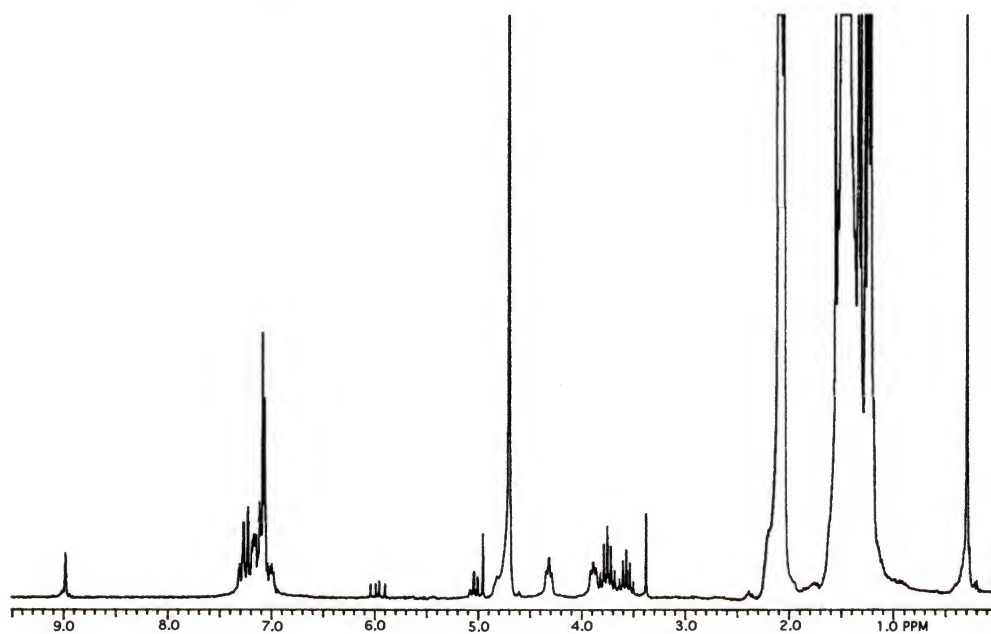


Figure 3-18. Attempted metathesis of methylenecyclohexane 37, where [M] represents catalyst 15 or 16.

Although methylenecyclohexane 37 did not dimerize in the presence of either catalyst 15 or 16, the ^1H NMR monitored interactions illustrate that these catalysts exhibit marked differences in activity towards 37. The molybdenum catalyst 16 appeared not to interact with methylenecyclohexane 37 at all. The persistence of the initial alkylidene (12.2 ppm),⁹³ coupled with the absence of both the proton signals corresponding to the release of the neophylidene (6.0 ppm) and ethylene (5.3 ppm) shows that the precatalyst remains intact (Figure 3-19). The tungsten catalyst 15 undergoes nonproductive metathesis with 37, releasing



a) ^1H NMR spectrum of **37** in the presence of the molybdenum catalyst **16** after 72 hr.



b) ^1H NMR spectrum of **37** in the presence of the tungsten catalyst **15** after 72 hr.

Figure 3-19. ^1H NMR spectral analysis of methylenecyclohexane **37** in the presence of catalysts **15** and **16**.

3-methyl-3-phenylbutene 26, demonstrated by the vinyl CH proton signal at 6.0 ppm, but the evolution of ethylene that accompanies the productive metathesis reaction is not observed. The ^1H NMR spectrum in Figure (3-19b) was taken at the end of 72 hr of reaction, at which time some of the initial alkylidene remains unreacted even though an excess of 37 is present, indicating the low reactivity of 37. However, the reaction of methylenecyclohexane 37 with the tungsten catalyst 15 demonstrates an increased reactivity when compared to the lack of reaction exhibited by 2,5-dimethyl-1,5-hexadiene 24, although the reactivity is not sufficient to support the productive metathesis reaction.

Attempted Metathesis of a Trisubstituted Exocyclic Alkene

Encouraged by the participation of methylenecyclohexane 37 in the nonproductive metathesis reaction, the metathetic activity of ethylenecyclohexane 38 was tested (Figure 3-20). While 38 has an increased degree of substitution over 37, it also is an internal

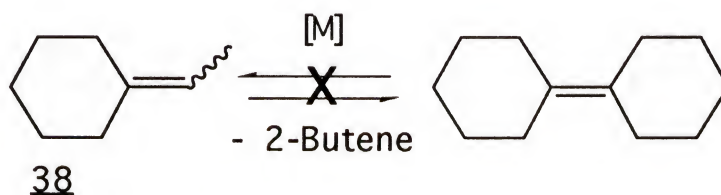


Figure 3-20. Attempted metathesis of ethylenecyclohexane 38, where [M] represents catalysts 15 or 16.

olefin, which are reported to be more reactive with the tungsten catalyst 15 than terminal olefins.⁸⁴ Ethylenecyclohexane tested the combined effects of the increased reactivity of the internal olefin

with the lowered steric interaction of the six membered ring as 1,1-disubstituent.

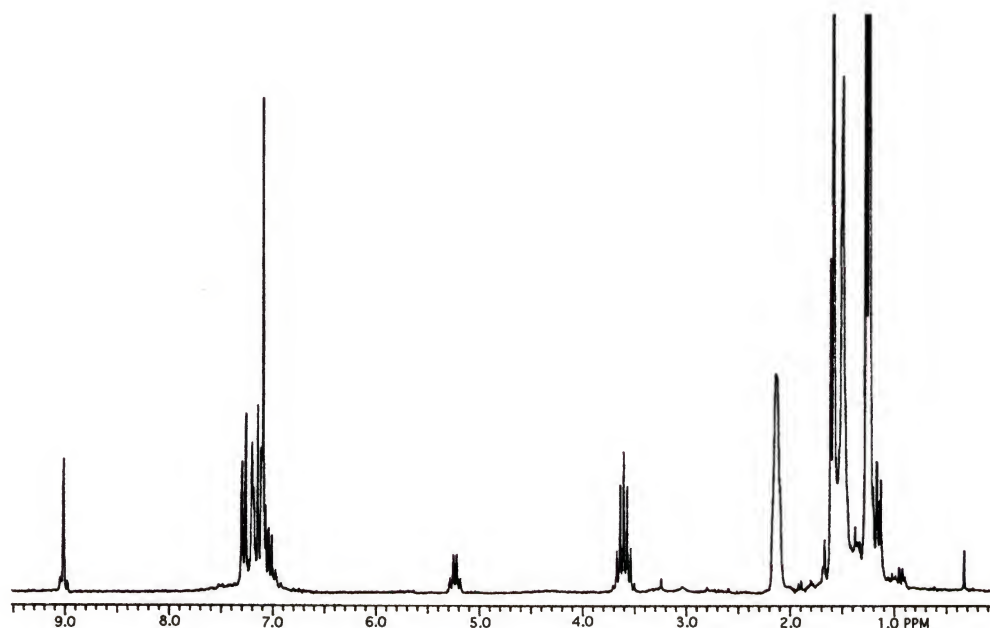


Figure 3-21. ¹H NMR spectrum of ethylenecyclohexane 38 in the presence of the tungsten catalyst 15 after 72 hr.

Neither catalyst 15 nor 16 produced any productive metathesis with 38. The ¹H NMR spectra of these solutions after 72 hr, exhibited no interaction of the original alkylidene of either catalyst with 38 (Figure 3-21). The attempted activation of the tungsten catalyst 15 towards the metathesis of 38 by adding ethylene to the solution failed to bring about productive metathesis as well. Obviously, any gain in reactivity resulting from the methyl substituent is far outweighed by the increased steric bulk about the functional group.

Conclusions of the 1,1-Disubstituted Olefin Model Study

This model compound study of the olefin metathesis reactivity of 1,1-disubstituted and trisubstituted alkenes with catalysts 15 and 16 demonstrates the steric influence exerted by the alkyl substituent of the olefin. The disproportionation of the trimethyl substituted alkene 32 results in an equilibrium distribution of reactants and products (Table 3-1), while all attempts at metathesizing trisubstituted olefins containing even one larger alkyl substituent failed.

The activities of the two different catalysts 15 and 16 with respect to the metathesis of 1,1-disubstituted and trisubstituted is similar, as neither catalyst affords the homometathesis of such alkenes. In fact, the formation of the 1,1-disubstituted alkylidene is not observed with either catalyst.

In contrast, the molybdenum catalyst 16 showed an enhanced reactivity over the tungsten catalyst 15 towards the transmetathesis between an internal olefin (1,2-disubstituted) and a 1,1-disubstituted alkene (Figure 3-8). The molybdenum catalyst 16 produces trisubstituted olefins from this transmetathesis reaction, while the tungsten catalyst 15 is ineffective.

Alternating Copolymer Synthesis

The selectivity exhibited by the tungsten catalyst 15 in the metathesis of 2-methyl-1,5-hexadiene 27 provided an opportunity to synthesize alternating copolymers with ADMET polymerization techniques. Catalyst 15 selectively and quantitatively metathesized

the vinyl groups of 24 while leaving the methyl substituted alkene unreacted (Figure 3-5). Since this catalyst lacks the ability to form tri- and tetra-substituted olefins, such functionalities were predicted to remain inert during polymerization, especially in the presence of reactive vinyl groups.

Alternating copolymers are usually synthesized by the radical polymerization of two monomers of opposite polarity through the initial formation of a charge transfer complex. Since pure hydrocarbon monomers generally possess similar electronic properties, they tend to form randomly distributed copolymers, showing no tendency towards alternation. Thus, the alternating copolymers of different dienes are relatively unknown.

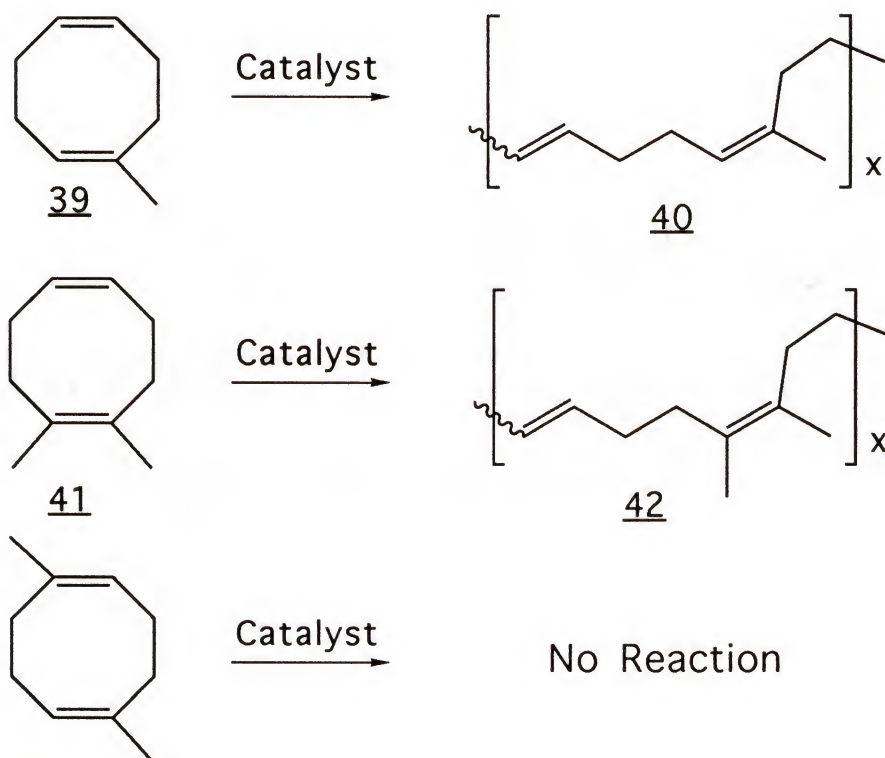


Figure 3-22. ROMP of unequally substituted cyclic dienes producing alternating copolymer structures.¹⁰⁵

The application of the olefin metathesis reaction to the synthesis of alternating hydrocarbon polymers was first reported by Ofstead for the ring opening metathesis polymerization of a series of unequally substituted cyclooctadienes (Figure 3-22),¹⁰⁵ such as 1-methyl-1,4-cyclooctadiene 39, 1-ethyl-1,4-cyclooctadiene, 1-chloro-1,4-cyclooctadiene, and 1,2-dimethyl-1,4-cyclooctadiene 41. In each case, the polymerization proceeded predominately through the metathesis of the unsubstituted olefin, thus providing an alternating copolymer structure.

Applying the same rationale to ADMET polymerization chemistry, through the proper design of monomers the selectivity exhibited by the tungsten catalyst 15 was exploited in the synthesis of perfectly alternating hydrocarbon copolymers.

Polymerization of 5-methyl-1,5,9-decatriene

5-Methyl-1,5,9-decatriene 43 is the acyclic diene analog of 1-methyl-1,4-cyclooctadiene 39, and this compound 43 was used to synthesize an alternating copolymer containing the repeat units of isoprene and 1,3-butadiene (Figure 3-23).

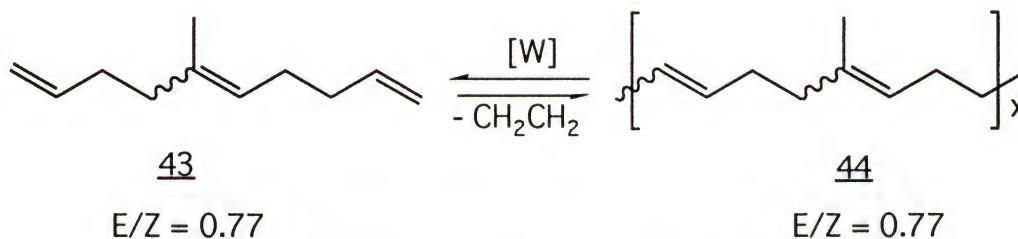
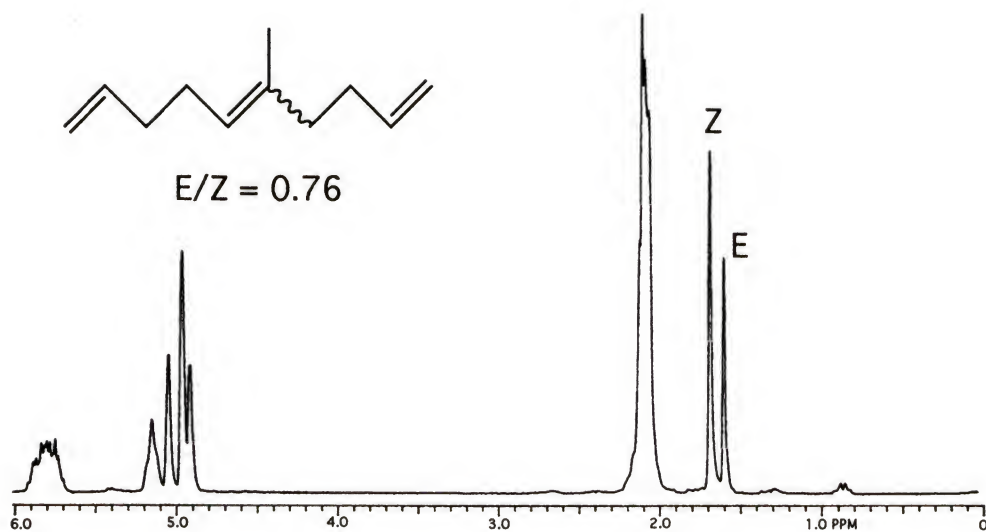
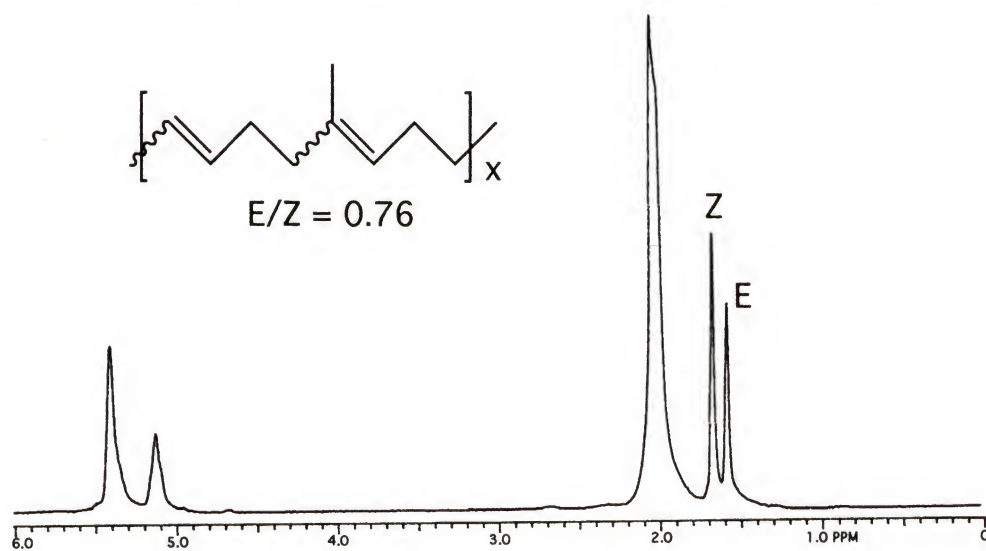


Figure 3-23. ADMET polymerization of 5-methyl-1,5,9-decatriene 43, producing the alternating copolymer of isoprene and 1,3-butadiene, where E/Z refers to the ratio of stereochemical isomers of the isoprene unit and $[W]$ represents catalyst 15.



a) ^1H NMR spectrum of 5-methyl-1,5,9-decatriene 43.



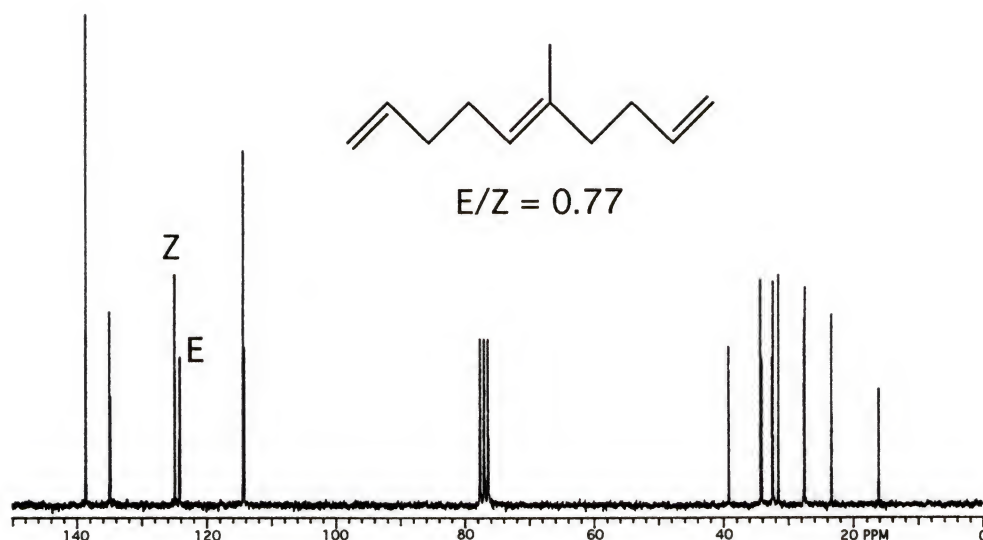
b) ^1H NMR spectrum of poly(butadiene-*a*-isoprene) 44.

Figure 3-24. ^1H NMR spectral analysis of 5-methyl-1,5,9-decatriene 43 polymerization.

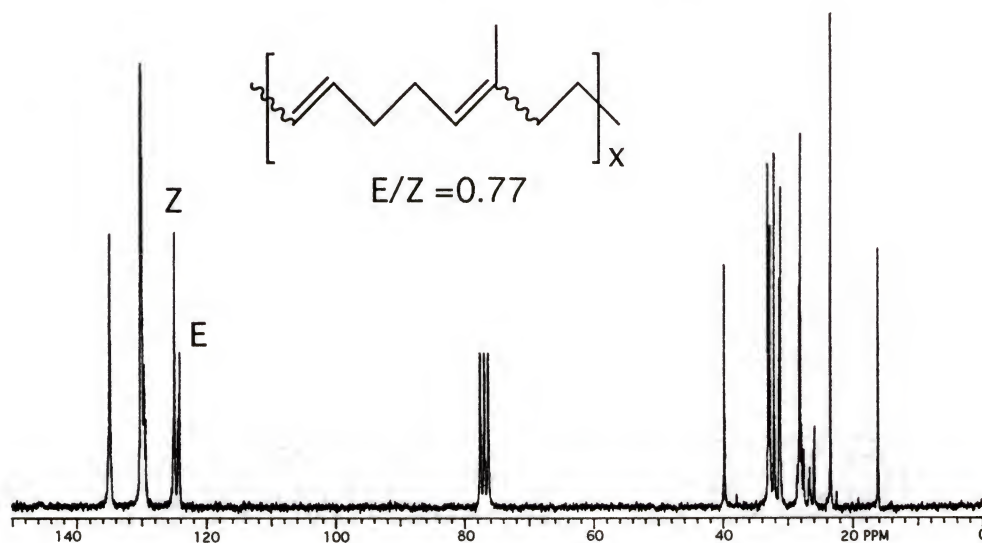
Polymerization occurs exclusively through the metathesis of the vinyl groups, resulting in the alternating polymer structure 44. Any deviation in the alternating sequence of this polymer would require the formation of a tetrasubstituted alkene where two of the four substituents would be the polymer backbone; catalyst 15 has not demonstrated any capability of producing such an olefin.

Monitoring the stereochemistry of the isoprene unit confirmed the alternating structure of polymer 44. The methyl protons of the isoprene structure, both in the monomer and in the polymer, produce a proton signal at 1.7 ppm for the Z isomer, and at 1.6 ppm for the E isomer (Figure 3-24b).¹⁰⁰ The stereochemistry of the isoprene unit in the polymer 44 remained unchanged from the monomer with an E/Z isomer ratio of 0.76, which implies that this bond did not participate in the olefin metathesis reaction.

Quantitative ^{13}C NMR also confirmed that the stereochemistry of the isoprene unit had been maintained throughout the polymerization. The methine carbon of the isoprene unit produces two distinct carbon signals for each isomer, Z at 124.9 ppm and the E at 124.1 ppm.¹⁰¹ The E/Z ratio determined was 0.77 for both the monomer and the polymer. Retention of stereochemistry about the substituted olefin indicates that this bond had not participated in the olefin metathesis reaction, and that the polymer structure 44 is a perfectly alternating copolymer of isoprene and 1,3-butadiene.



a) Quantitative ^{13}C NMR spectrum of 5-methyl-1,5,9-decatriene **43**.



b) Quantitative ^{13}C NMR spectrum of poly(5-methyl-1,5,9-decatriene) **44**.

Figure 3-25. Quantitative ^{13}C NMR analysis of the polymerization of 5-methyl-1,5,9-decatriene **43**, where E/Z refers to the stereochemical isomer ratio of the isoprene unit.

Polymerization of 5,6-dimethyl-1,5,9-decatriene

The ADMET polymerization of 5,6-dimethyl-1,5,9-decatriene 45 also produces an alternating copolymer with catalyst 15. Polymer 46 is analogous to the polymer produced from the ROMP of 1,2-dimethyl-1,4-cyclooctadiene (Figure 3-26). Any participation

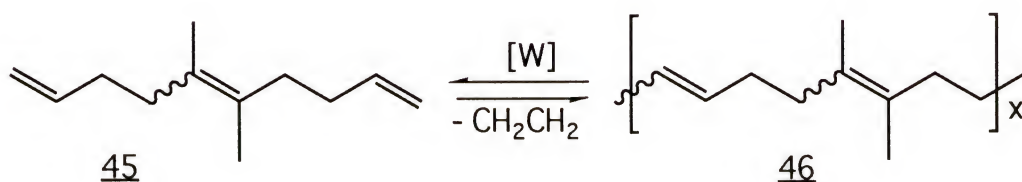


Figure 3-26. ADMET polymerization of 5,6-dimethyl-1,5,9-decatriene 45 to the alternating copolymer structure 46.

of the tetrasubstituted olefin in the transmetathesis reaction would have resulted in the formation of isoprene units, which are known to possess methine carbons with chemical shifts at 124.9 and 124.1 ppm.¹⁰¹ The quantitative ¹³C NMR of the polymer produced from the ADMET polymerization of 5,6-dimethyl-1,5,9-decatriene 46 exhibits no carbon resonances in this area of the spectrum, which indicates that the tetrasubstituted olefin did not participate in the metathesis reaction, and that this polymer also possesses a perfectly alternating structure (Figure 3-27).

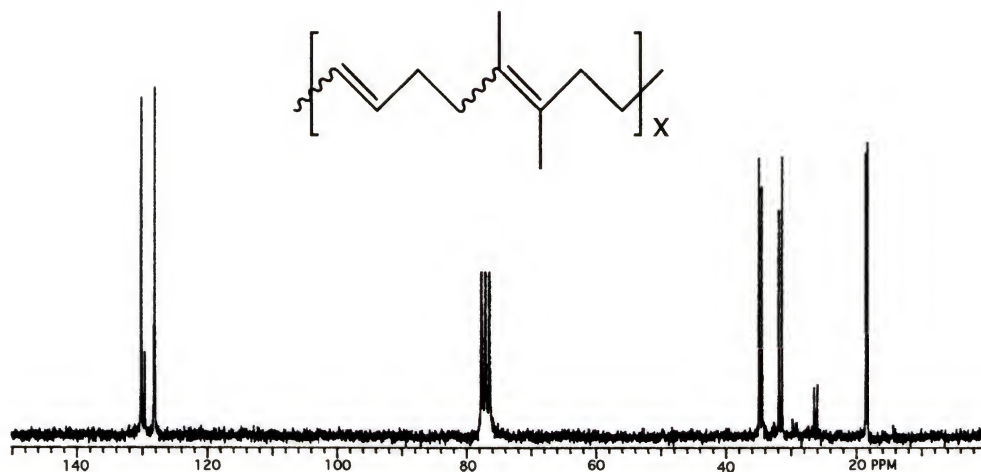


Figure 3-27. Quantitative ^{13}C NMR spectrum of poly(5,6-dimethyl-1,5,9-decatriene) 46.

Polymerization of 5,6-diphenyl-1,5,9-decatriene

The ADMET comonomer 5,6-diphenyl-1,5,9-decatriene provided the synthetic route to a previously unknown polymer, and simultaneously, an opportunity to verify the alternating nature of this polymerization through the use of ultraviolet spectroscopy. Like stilbene, 47 possesses a large molar extinction coefficient, 9700 L/(mol cm) at 247 nm, that can be used to monitor the participation of this substituted olefin in the olefin metathesis

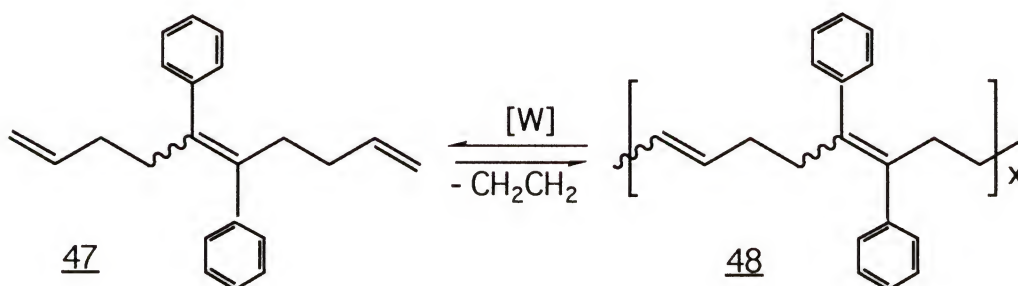


Figure 3-28. ADMET polymerization of 5,6-diphenyl-1,5,9-decatriene 47, where [W] represents catalyst 15.

reaction. A hypsochromic shift in the UV spectrum would accompany any transmetathesis of the tetrasubstituted olefin, as the conjugation of the stilbene-like structure is replaced with a styrene-like olefin. Figure (3-29) shows the UV spectrum of the two equal concentration solutions of both the monomer 47 and the polymer 48, where the concentration of the polymer was based upon the molecular weight of the repeat unit. The fact that these spectra are essentially identical is the strongest evidence for the perfectly alternating structure of polymer 48.

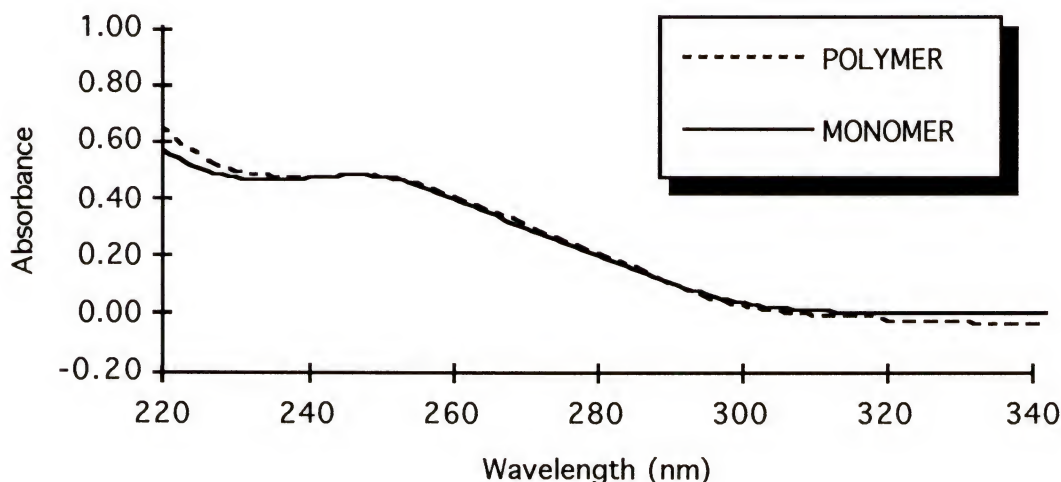


Figure 3-29. UV spectra for 5,6-diphenyl-1,5,9-decatriene 47 and the corresponding alternating copolymer 48. Solutions are of equal concentration (polymer concentration based upon repeat unit) in pentane.

Table 3-2. Characterization Data of Alternating Copolymers Synthesized via ADMET Polymerization					
Polymer	\bar{M}_n (SEC) ($\times 10^3$)	\bar{M}_n (VPO) ($\times 10^3$)	PDI	T_g (°C)	TGA (°C)
23	13	13	2.0	-58	378
25	11	11	1.9	-54	365
27	6.6	6.3	1.9	21	373
SEC-	Size Exclusion Chromatography, relative to polybutadiene standards, g/mol				
VPO-	Vapor Pressure Osmometry, calibrated with sucrose octaacetate, g/mol				
PDI-	Polydispersity Index = \bar{M}_w / \bar{M}_n				
T_g -	Glass transition temperature measured by differential scanning calorimetry at a heating rate of 10 °C/min				
TGA-	Thermogravimetric Analysis, onset °C under nitrogen flow, heating rate = 10 °C/ min				

The spectral analysis of the polymers 44, 46 and 48, coupled with the reactivity rules developed in the model compound study, strongly support the 'perfectly alternating' nature of these polymers. These alternating polymer syntheses are examples of how negative results, in this case lack of reactivity, can be exploited as an advantage. A number of alternating copolymers are possible from this reaction scheme; one needs only design the monomers with the reactivity of the olefin in mind.

CHAPTER 4

THE METATHESIS ACTIVITY OF ALPHA SUBSTITUTED OLEFINS

The previous chapter discusses the effect of alkyl substitution at the olefin sp^2 carbon on the metathesis activity as it pertains to ADMET polymerization. In this chapter, both mono- and dienes were employed for the model study to investigate the steric influence on the olefin metathesis activity of alkenes that possess branching at the allylic carbon atom. Since the olefins employed for this study were both vinylic and internal, the alkyl chain was labeled starting adjacent to the functional alkene (Figure 4-1). Accordingly, the

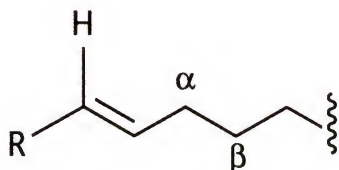


Figure 4-1. Labeling scheme for substitution study presented in this chapter. R = methyl or hydrogen

effects of substitution (branching) at the alpha carbon on the metathesis activity of hydrocarbons have been investigated, with the ultimate goal of the model study being to define the relevance of α -branched olefins to ADMET polymerization chemistry.

The Alpha-Methyl Substitution Effect on Metathesis
Activity of Dienes

The metathesis activity of 3-methyl-1,4-pentadiene 49 with the tungsten catalyst 15 has been studied, in an effort to investigate the steric influence of an allylic methyl substituent on the metathesis activity of acyclic dienes. Since the formation of the six-membered ring is energetically favored, 49 was not expected to polymerize, but dimerize to 2,6-dimethyl-1,4-cyclohexadiene (Figure 4-2). However, no evidence of productive metathesis was observed after repeated attempts, as only 3-methyl-1,4-pentadiene was isolated.

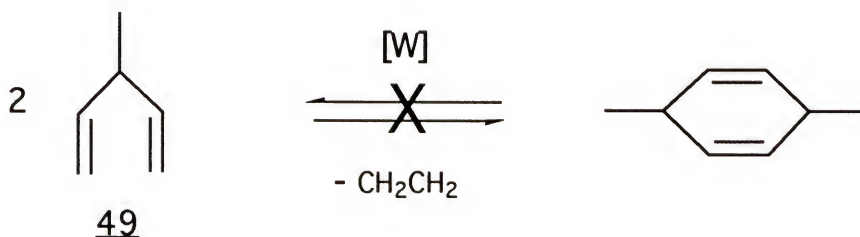


Figure 4-2. Expected cyclization dimerization of 3-methyl-1,4-pentadiene 49, [W] represents catalyst 15.

The lack of productive metathesis activity demonstrated by 49 cannot be attributed solely to the steric influence of the allylic methyl substituent, since the influence of the proximity of the two olefins in 49 had not been elucidated. The presence of lone electron pairs in close proximity to the reactive alkylidene often impedes the metathesis activity of alkenes. For example, the lone electron pairs of amines and esters have the ability to coordinate to the catalyst metal center preventing productive metathesis, a phenomenon

recently termed the 'negative neighboring group effect' and illustrated in Figure (4-3a and b).⁶⁸ Since the location of pi electrons along the alkyl chain of a reactive olefin also affect the

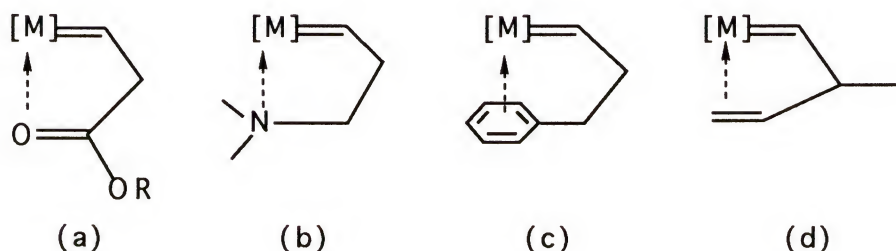


Figure 4-3. Coordination of additional nucleophilic center effecting the reactivity of the alkylidene, (a),¹⁰⁶ (b),¹⁰⁷ (c),¹⁰⁸ [M] represents the catalyst metal center.

reactivity of the olefin coordinated to the metal center (Figure 4-3c)¹⁰⁸, it is possible that the alpha methyl substituent is not responsible for the lack of metathesis activity of 49, but that the second vinyl group is coordinating to the catalyst metal center and preventing the productive metathesis reaction (Figure 4-3d).

Metathesis Activity of Alpha-Methyl Substituted Monoenes

The metathesis activity of 3-methylhexene 50 was tested in order to distinguish between the two possible causes of inactivity for 49, since 50 contains only one olefin (Figure 4-4a). In fact, no productive metathesis of 50 was observed with the tungsten catalyst 15, and it was concluded that the presence of an allylic methyl group alone is enough to prevent productive metathesis of a vinyl group.

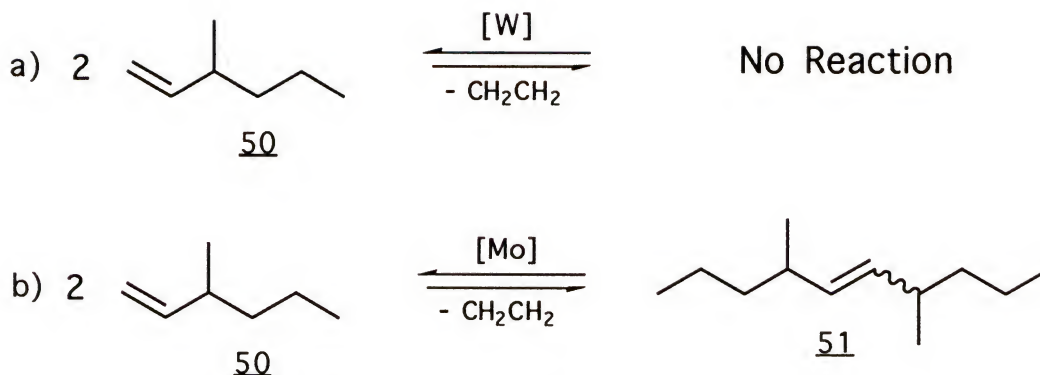


Figure 4-4. Metathesis of 3-methylhexene where [W] represents the tungsten catalyst 15 and [Mo] represents the molybdenum catalyst 16.

However, use of the molybdenum catalyst 16 in the metathesis of 50 resulted in the quantitative conversion to 4,7-dimethyl-5-decene 51 (Figure 4-4b). This result was not surprising considering the success demonstrated by catalyst 16 in metathesizing the 1,1-disubstituted olefins discussed in Chapter 3. The difference in reactivity displayed here by the molybdenum 16 and tungsten 15 catalysts is discussed later in this chapter.

Metathesis of Non-Equivalent Substituted Dienes

Although no productive metathesis activity was detected when the tungsten catalyst 15 was added to 3-methylhexene 50, it had not been determined that the catalytic species had actually been generated. Since the metathesis 'catalysts' employed for this study are actually a pre-catalysts, the catalytic species is generated in situ by reaction of the initial alkylidene with the alkene reactant (Figure 3-7). The steric interaction of the initial alkylidene

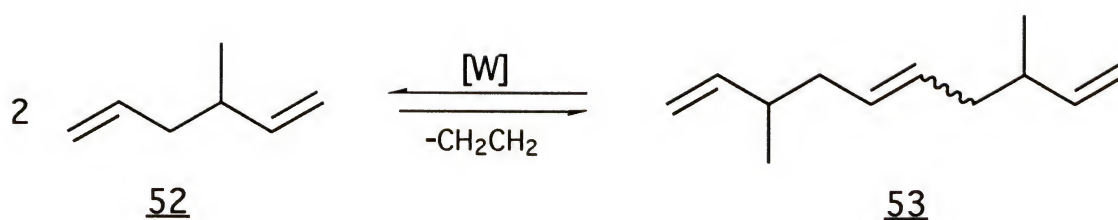
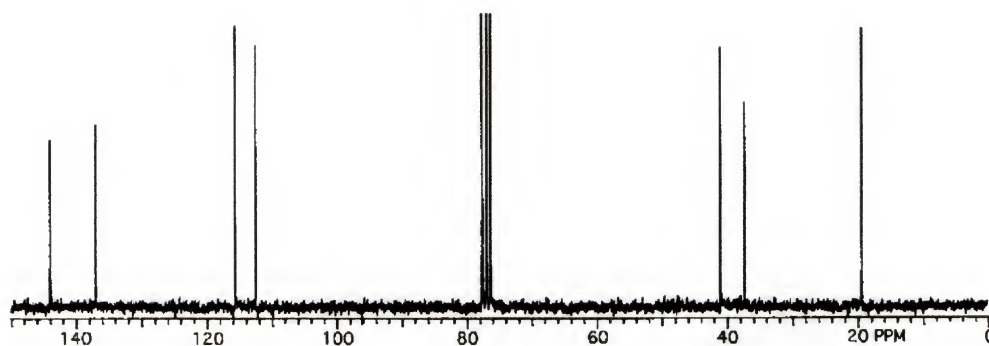


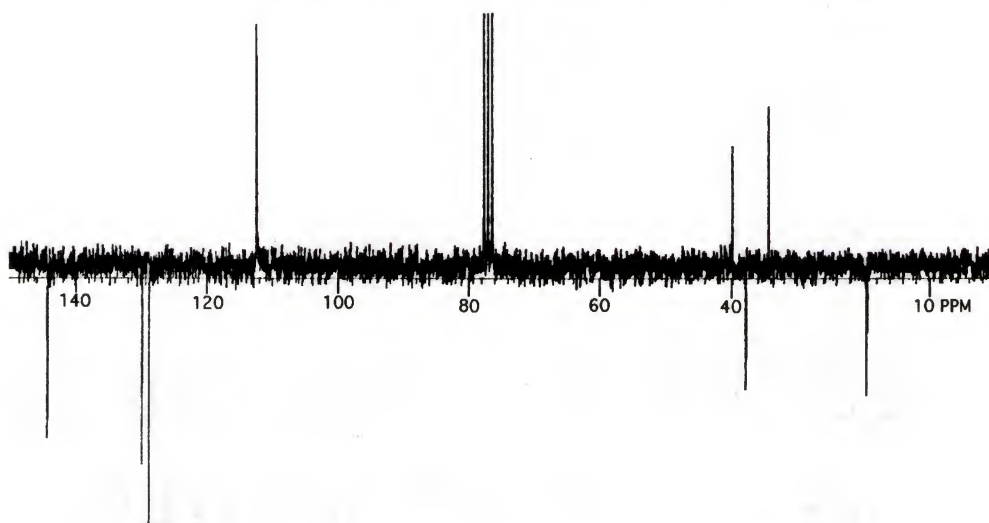
Figure 4-5. Metathesis of 3-methyl-1,5-hexadiene 52 to produce the dimer 3,8-dimethyl-1,5,9-decatriene, 53. where [W] represents the tungsten catalyst 15.

(neophyl) with the alpha methyl vinyl group might have prevented the formation of the catalytic alkylidene. In order to draw any specific conclusions about the reactivity of the alpha methyl substituted vinyl group, the catalytic alkylidene had to be generated in the presence of this alpha olefin. For this purpose, 3-methyl-1,5-hexadiene 52 was exposed to the tungsten catalyst 15 under ADMET reaction conditions (Figure 4-5). This is an appropriate diene for this study, since it possesses both an alpha and a beta substituted vinyl group. The metathesis of the beta substituted olefin serves as an indicator of catalyst activity while generating the methylidene.

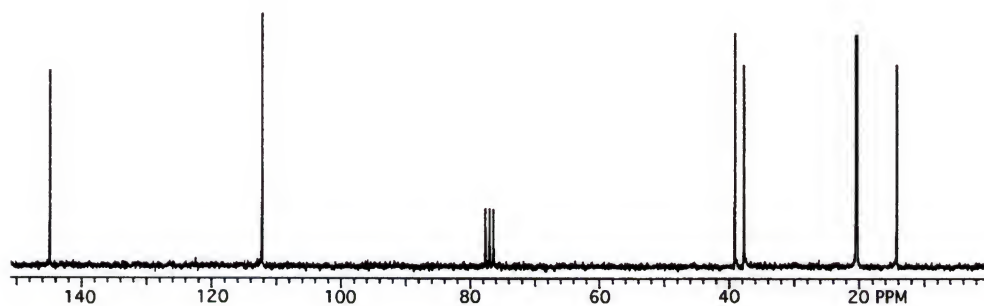
Compound 52 did show productive metathesis activity, generating dimer 53. Comparison of the ¹³C NMR spectrum of 53 (Figure 4-6b) with the spectrum of 3-methylhexene 50 (Figure 4-6c) provided the information needed to determine which of the two vinyl groups had metathesized.



a) ^{13}C NMR spectrum of 3-methyl-1,5-hexadiene 52.



b) ^{13}C NMR spectrum of 3-methyl-1,5-hexadiene dimer:
3,8-dimethyl-1,5,9-decatriene 53.



c) ^{13}C NMR spectrum of 3-methylhexene 50.

Figure 4-6. ^{13}C NMR analysis of 3-methyl-1,5-hexadiene 52
metathesis with the tungsten catalyst 15.

The vinyl carbon resonances remaining in the spectrum of the dimer 53 (Figure 4-6b) match the chemical shifts for the vinyl group of 3-methylhexene 50 (Figure 4-5c), and shows that metathesis had occurred exclusively at the beta substituted vinyl group to yield 3,8-dimethyl-1,5,9-decatriene 53. The alpha substituted vinyl group remained inert to the tungsten catalyst 15 throughout the reaction.

There is no doubt that the catalytic alkylidene had been generated in the metathesis of 52, and yet no metathesis of the alpha substituted olefin was observed. The absence of the cross metathesis product of the two different vinyl groups was surprising, but totally unexpected was the less than quantitative conversion of the beta substituted vinyl group (32%). Neither increasing the catalyst concentration nor the reaction time was successful in increasing the extent of conversion. Although it is certain that the catalytic species was present in solution, it can be argued that the lack of productive metathesis of the alpha substituted olefin was due to competition with the beta substituted vinyl group.

Specific Interaction of Alpha-Methyl Vinyl Groups with the Tungsten Catalyst

Further insight into the results of the alpha methyl substituted vinyl reactions was gained when the solution reaction of 3-methylhexene 50 with the tungsten catalyst 15 was monitored by ^1H NMR (Figure 4-8). The ^1H NMR spectra of this reaction after 72 hr. (Figure 4-7) illustrates that 3-methylhexene 50 exchanges with

the initial alkylidene 15 (Figure 4-8) through a degenerate metathesis reaction, where the tungsten metallacycle generated must be α - α' disubstituted 54. During the course of this reaction, the alkylidene proton signal (9.1 ppm) is consumed while the release of 3-methyl-3-phenylbutene 26 is evident from the new vinyl proton signals at 6.0 ppm (dd, CH).¹⁰⁹ Since no new alkylidene proton signal is observed, the newly generated alkylidene 55 must react with another molecule of 3-methylhexene 50 to form either the α - α' metallacycle 56 or the α - β disubstituted metallacycle 57, or both (Figure 4-8). The alpha protons of these metallacycles are lost in

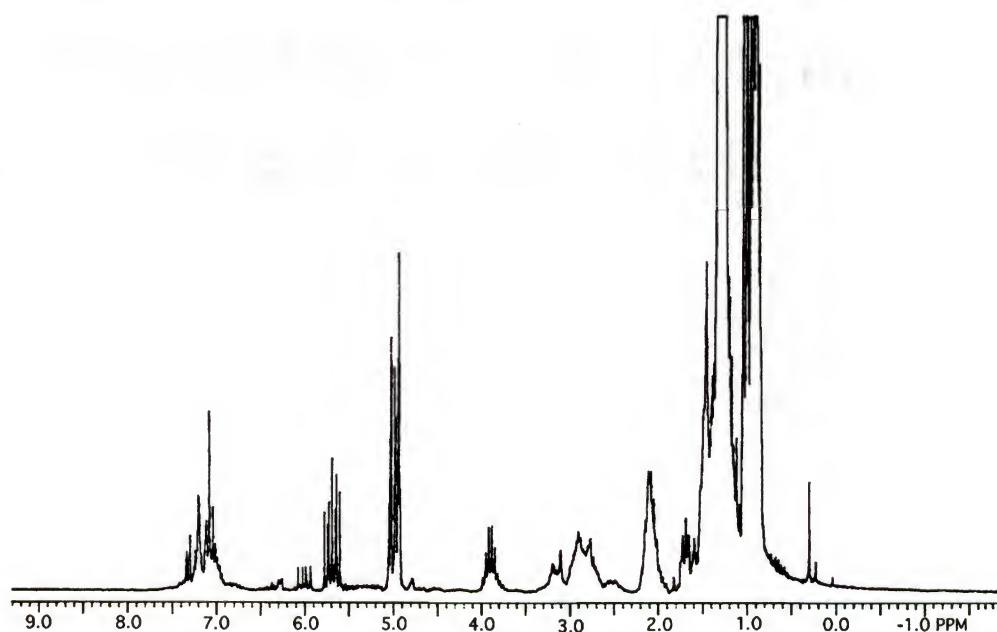


Figure 4-7. ^1H NMR of 3-methylhexene 50 with tungsten catalyst 15 after 72 hr.

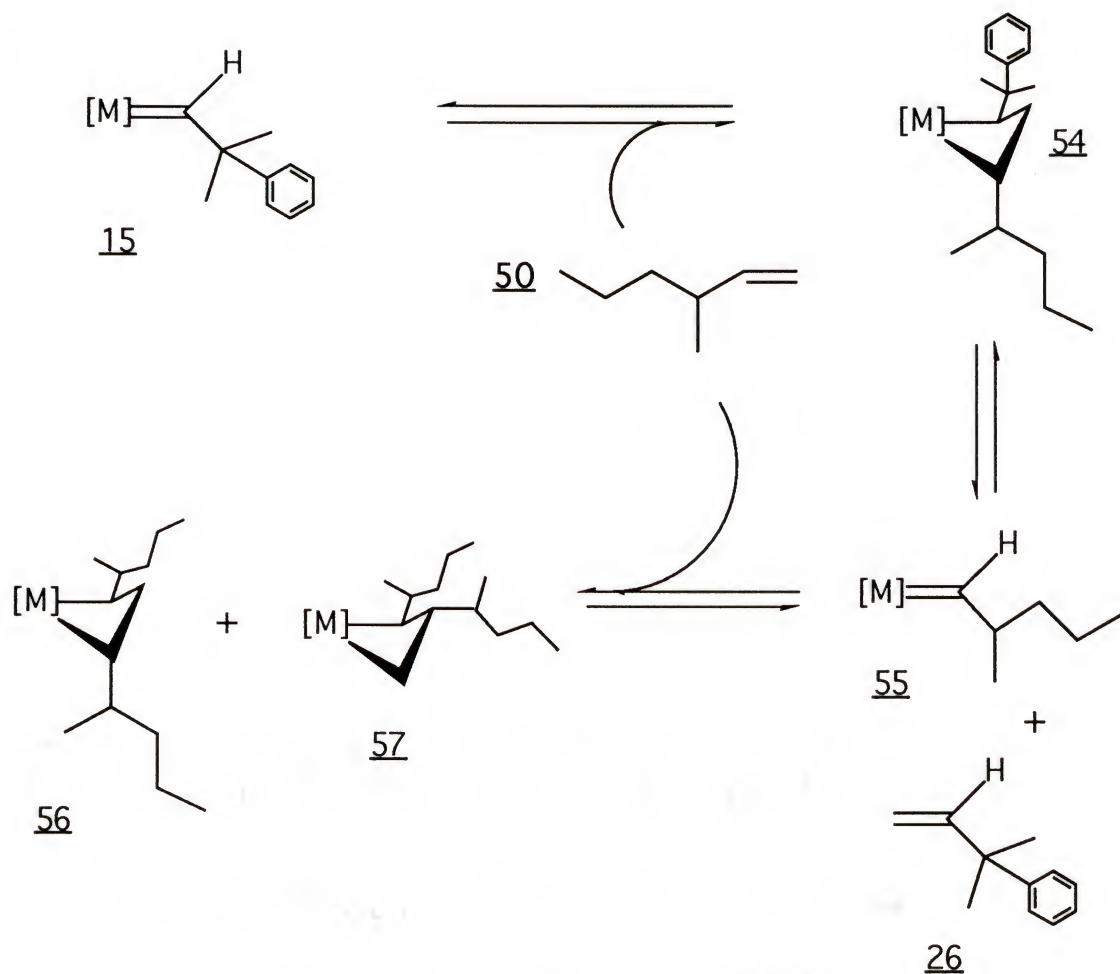


Figure 4-8. Illustration of the degenerate metathesis of 3-methylhexene 50, where [M] represents the tungsten catalyst 15.

the alkyl region of the NMR spectra, but the beta protons are detected between 2.5 and 3.2 ppm (Figure 4-7).⁸⁴ Although the structure of the metallacycle present is not clearly defined in the ¹H NMR spectrum, metallacycle 56 can only result in degenerate metathesis, thus regenerating the alkylidene 55, while the only route to productive metathesis is metallacycle 57 which, if formed, does not release the olefin 4,7-dimethyl-5-decene 51 (Figure 4-4a).

The location of the beta hydrogen signals in the ^1H NMR (2.5-3.2 ppm) indicates that the metallacycles possess a square pyramidal geometry.¹¹⁰ In addition, no trigonal bipyramidal metallacycle is detected as indicated by the absence of any proton resonances upfield from tetramethylsilane.

The absence of the trigonal bipyramidal metallacycle offers an explanation why no productive metathesis is observed for 3-methylhexene 50 in the presence of the tungsten catalyst 15. Schrock *et al.* have shown that trigonal bipyramidal and square pyramidal metallacycles interconvert on the NMR time scale at room temperature for this same catalyst.¹¹⁰ The proposal has been made that the addition and loss of an olefin with the catalyst center proceeds through the trigonal bipyramidal conformation, and that the square planar conformation is most likely the intermediate that allows for the exchange of olefins.⁸⁴ Therefore, a square pyramidal metallacycle complex must rearrange to form a trigonal bipyramidal metallacycle before an olefin can be lost.

The metallacycle formed from the reaction of 3-methylhexene 50 with the tungsten catalyst 15 possesses a square pyramidal geometry. The ^1H NMR data suggests that the trigonal bipyramidal geometry for metallacycle 57 is unfavorable due to the steric interaction of the alpha branched alkyl groups of both substituents of the metallacycle. This steric constraint may arise from the metallacycle substituents interacting with each other, with the ligands of the catalyst, or both. The stability of metallacycles 56 and 57, relative to the metallacycles of productive metathesis reactions is indicated by the absence of any alkylidene proton

signals; the reaction of *cis*-2-pentene with catalyst 15 possesses a butenylidene at room temperature,⁸⁴ whereas the reaction of 3-methylhexene shows only metallacycle at temperatures up to 50 °C, in addition to the absence of the trigonal bipyramidal metallacycle.

The stability of the tungsten metallacycle produced from the reaction of 3-methylhexene 50 with catalyst 15, whether it is α,β or the α,α' -disubstituted, explains why the metathesis of 3-methyl-1,5-hexadiene 51 is less than quantitative. Catalyst 15 is consumed by the alpha methyl vinyl groups and trapped in the stable metallacycle, thus slowing the productive metathesis of the beta substituted vinyl groups.

Metathesis Activity of Metallacycle Formed from 3-Methylhexene and the Tungsten Catalyst

The tungsten catalyst 15 is not completely deactivated by the reaction with 50, as is demonstrated by the metathesis of 1,9-decadiene 5 by the catalyst residue produced by the reaction of 3-methylhexene 50 with catalyst 15. Qualitatively, a typical ADMET reaction of 1,9-decadiene produces crystalline polymer within four hours after addition of the tungsten catalyst 15, but the 3-methylhexene pre-exposed catalyst produces only liquid oligomers of 1,9-decadiene after one week of reaction. The stability of the metallacycle 56 or 51 significantly slows the productive metathesis of unsubstituted olefins, thus explaining the less than quantitative metathesis of the beta substituted vinyl group in the reaction of 3-methyl-1,5-hexadiene 52 with catalyst 15.

Steric Influence on Metallacycle Formation

An additional explanation for the lack of metathesis activity exhibited by the alpha methyl substituted olefins 50 and 52 focuses on the approach of the second olefin to the active alkylidene. The α,β -disubstituted metallacycle 57 may not form due to the steric interaction between the alpha branched alkyl chain of the approaching olefin and the alkylidene 55 with its branched alkyl chain. If this interaction is sufficient, the only metallacycle formed may be the α,α' -disubstituted metallacycle 56, which is only capable of degenerate metathesis. The predominance of the degenerate metathesis reaction explains the absence of new product formation for 3-methylhexene 50, as well as the slowed metathesis observed for 3-methyl-1,5-hexadiene 52. Isolation of the metallacycle from these reactions would clarify each of the above explanations, but so far isolation of this species has remained an elusive task.

Difference in Catalytic Activity of the Tungsten and Molybdenum Catalysts

Traditionally, tungsten metathesis catalysts are perceived as more reactive and less selective than the molybdenum analogs.³ From the information known about metathesis catalysts of both of these metals, both classical and Lewis acid free types, two explanations accounting for the difference in metathesis activity demonstrated by the alpha methyl substituted alkenes with catalysts 15 and 16 present themselves. Since molybdenum catalysts are expected to be less electrophilic than their tungsten analogs, it is likely that loss of an olefin from the metallacycle is

more favorable when the metal is molybdenum, and thus occurs more readily with bulky substituents for catalyst 16 as compared to catalyst 15. Along the same rationale, the molybdenum methyldiene 25b should be more stable than the tungsten version 25a, thus increasing the likelihood of productive metathesis for the molybdenum catalyst over the tungsten catalyst.^{84,93}

The metallacycles of molybdenum have also been reported as being less stable than tungsten metallacycles, which has been attributed to the shorter metal carbon bond for molybdenum as compared to tungsten.^{84,93} Thus, the steric interaction of the metallacycle substituents with the ligands on the metal center may provide the necessary driving force that allows the molybdenum catalyst to metathesize sterically encumbered olefins while the tungsten catalyst does not.

Metathesis of Alpha-Ring Substituted Vinyl Groups

Most attempts to metathesize alpha substituted vinyl alkenes with the tungsten catalyst 15 have failed, with the one exception being the initial model study performed on styrene compounds, in which various substituted styrenes were successfully dimerized to the corresponding substituted stilbenes with the neopentyl version of the tungsten catalyst 1c.⁵⁹ While the planarity of the benzene ring may lower the steric constraints of this reaction, electronic effects cannot be ruled out. Thus, model compounds containing rings alpha to an olefin were investigated for productive metathesis activity under ADMET reaction conditions, with the goal of relieving

the steric constraints of the metathesis of alpha substituted alkenes (Figure 4-9).

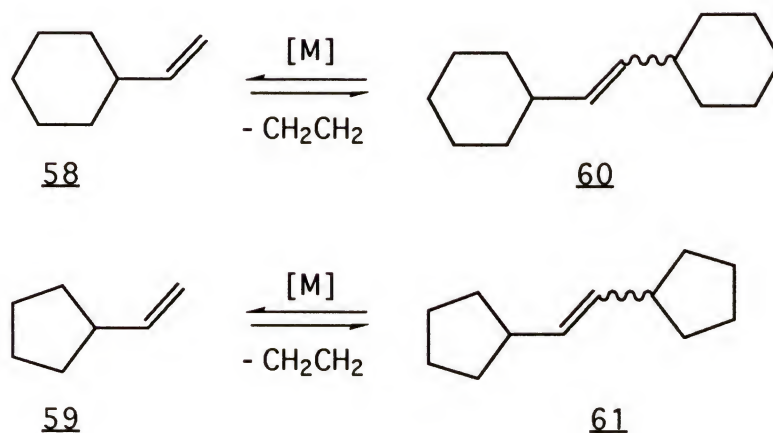
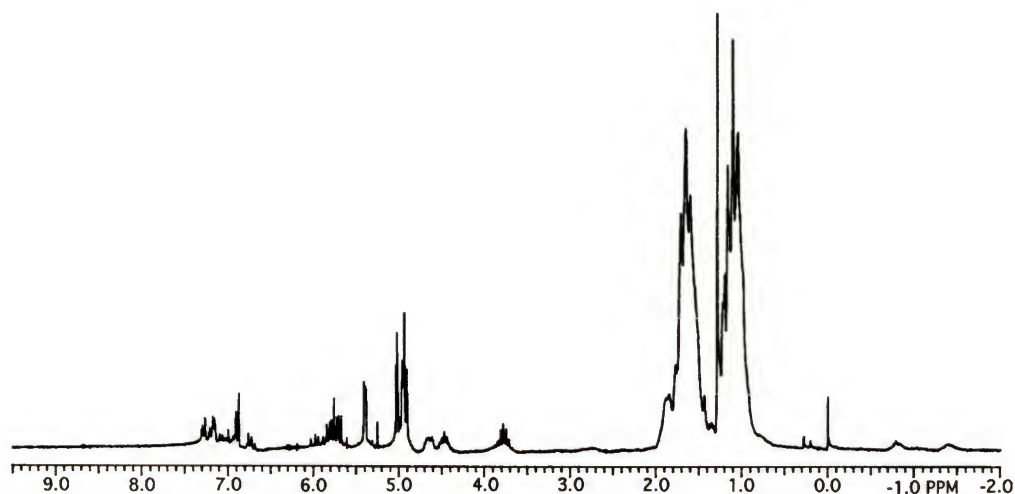


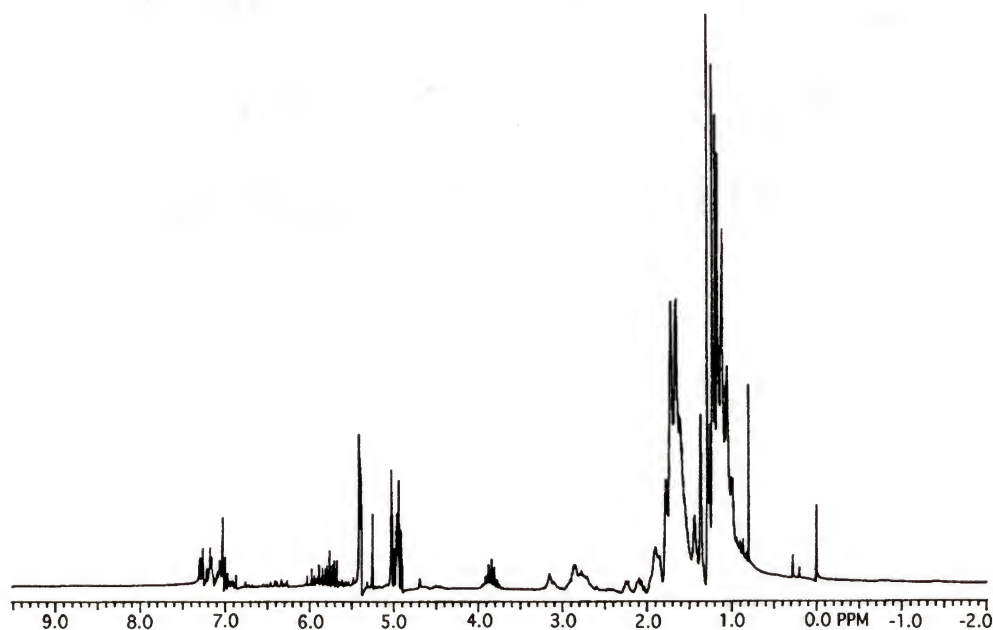
Figure 4-9. Metathesis of vinylcyclohexane 58 and vinylcyclopentane 59 to 1,2-dicyclohexylethene 60 and 1,2-dicyclopentylethene 61, respectively. $[M]$ represents catalysts 15 and 16.

Not surprisingly, vinylcyclohexane 58 and vinylcyclopentane 59 reacted quantitatively in the presence of the molybdenum catalyst 16 producing 1,2-dicyclohexylethene 60 and 1,2-dicyclopentylethene 61, respectively. The same products were obtained when the tungsten catalyst 15 was employed, however, the yields were less than 10% and did not improve with increased reaction time nor with increased catalyst concentration.

The solution reaction involving the tungsten catalyst 15 and vinylcyclohexane 58 demonstrates a remarkable difference from the reaction of 3-methylhexene 50, as evidenced by the proton NMR data (Figure 4-10). Initially, the tungsten metallacycle formed in the metathesis of vinylcyclohexane 58 is predominately trigonal



a) ^1H NMR of vinylcyclohexane 58 in the presence of the tungsten catalyst 15. Reaction time = 15 minutes



b) ^1H NMR of vinylcyclohexane 58 in the presence of the tungsten catalyst 15. Reaction time = 2 hr

Figure 4-10. ^1H NMR monitored reaction of vinylcyclohexane 58 with catalyst 15.

bipyramidal (proton signals upfield from tetramethylsilane), which are indicative of the unsubstituted metallacycle. After just 2 hr, only the square pyramidal metallacycle is evident (proton signals at 2.8 ppm and 3.2 ppm). 1,2-Dicyclohexylethene 60 is observed (internal olefin signal at 5.4 ppm)¹¹¹ along with ethylene (signal at 5.3 ppm). The low yields associated with the reaction of vinylcyclohexane 58 with the tungsten catalyst 15 may be a result of the stability of the square pyramidal metallacycle formed.

Metathesis of Alpha-Ring Substituted Internal Alkenes

Since the tungsten catalyst 15 is reported to be more reactive with internal olefins than with vinyl groups, alpha substituted olefins can be activated towards productive metathesis by employing a propenyl group in place of the vinyl functionality. The success of this approach was suggested by the reported metathesis of 4-methyl-2-pentene with the tungsten catalyst 15.⁸⁴ The fact that 4-methyl-2-pentene reacts with the tungsten catalyst, in comparison to the total lack of reactivity exhibited by

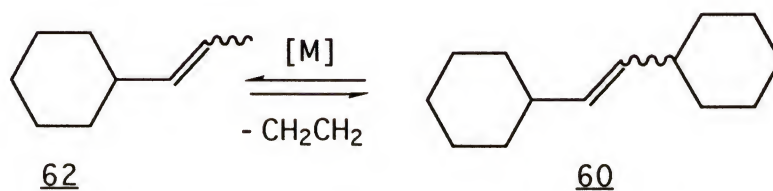


Figure 4-11. Metathesis of propenylcyclohexane where [M] represents catalyst 15.

3-methylhexene 50, encouraged the use of internal olefins with the tungsten catalyst 15. This approach was somewhat successful as

propenylcyclohexane 62 was metathesized in 80 % yield (Figure 4-11).

There are two possible explanations for the increased activity of propenylcyclohexane 62 over vinylcyclohexane 58. First, the internal olefin of 62 competes more effectively with the internal olefin of 1,2-dicyclohexylethene 60 for the metal center of the catalyst than does the corresponding vinyl group. Second, the propenylcyclohexane 62 always results in a trisubstituted

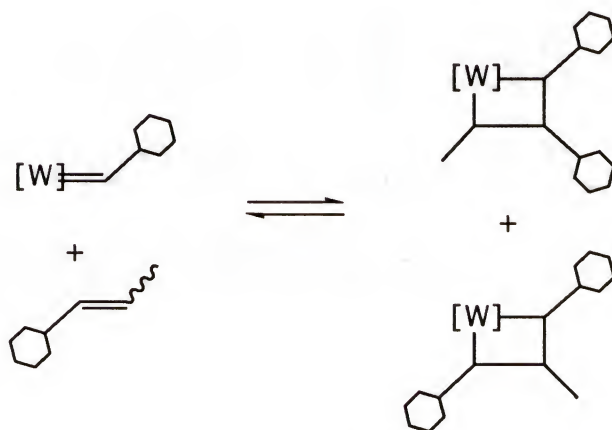


Figure 4-12. Illustration of the formation of trisubstituted metallacycles from propenylcyclohexane 62 and catalyst 15.

metallacycle, which are reported to be less stable than the mono- and di-substituted analogs (Figure 4-12).⁸⁴ Although an improvement in reactivity was observed, the metathesis of the propenylcyclohexyl functionality with catalyst 15 failed to meet the quantitative conversion requirement of ADMET polymerization chemistry.

Stereoselectivity of the Metathesis of Alpha-Substituted Olefins

The cis/trans ratio for 1,2-dicyclohexylethene 60 produced in this chemistry is 32 (97 % cis) when the tungsten catalyst 15 is used, and 54 (98 % cis) when the molybdenum catalyst 16 is used (Figure 4-13). A similar trend was established with the formation of 1,2-dicyclopentylethene 61; a cis/trans ratio of 12 (92 % cis) was obtained with the tungsten catalyst 15 and 13 (93 % cis) with the molybdenum catalyst 16. This trend of cis stereoselectivity in the metathesized olefin is consistent throughout all reactions where the olefin contains an alpha substituent (Table 4-1).

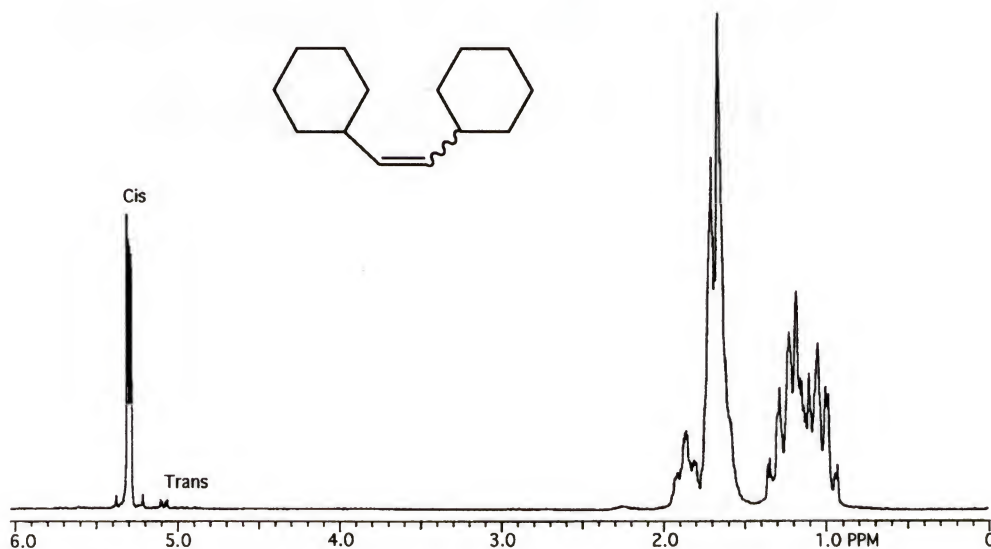


Figure 4-13. ^1H NMR spectrum of 1,2-dicyclohexylethene 60 produced from the metathesis of vinylcyclohexane with the molybdenum catalyst 16.¹¹¹

The high stereoselectivity exhibited in the metathesis products of the alpha substituted olefin reactions was surprising, since ADMET typically produces a trans content higher than the predicted thermodynamic equilibrium value for the metathesis of

unsubstituted linear olefins. The trans content found in the first ADMET polymerization of 1,9-decadiene was 93 %.⁵⁹ The stereoselectivity of the olefin metathesis reaction has been studied extensively,³ and the trans selectivity normally exhibited by ADMET polymerizations can be explained by the puckered ring metallacycle model originally proposed by Casey et al. (Figure 4-14).¹¹²

Table 4-1. Stereoselectivity of Metathesis Reactions					
Reactant	Product	Cat.	% <i>cis</i>	% <i>trans</i>	Ratio <i>c/t</i>
1,9-Decadiene	Polyoctenamer	W	7	93	0.08
3-Methylhexene <u>50</u>	4,7-Dimethyl- 5-decene <u>51</u>	Mo	60	40	1.3
Vinylcyclo- hexane <u>58</u>	1,2-Dicyclo- hexylethene <u>60</u>	W	97	2.9	33
Vinylcyclo- hexane <u>58</u>	1,2-Dicyclo- hexylethene <u>60</u>	Mo	98	1.7	58
Propenylcyclo- hexane <u>62</u>	1,2-Dicyclo- hexylethene <u>60</u>	W	97	2.7	35

Metallacycle 63, where both substituents are in a pseudoequatorial position on the ring, is preferred due to the lowest steric interaction between the alkyl substituents of the metallacycle ring, but as the substituents increase in size, this interaction becomes more significant. Since metallacycle 63 produces only the trans isomer, the stereoselectivity of ADMET chemistry emphasizes the importance of the interaction between the metallacycle ring substituents for the catalysts 15 and 16.

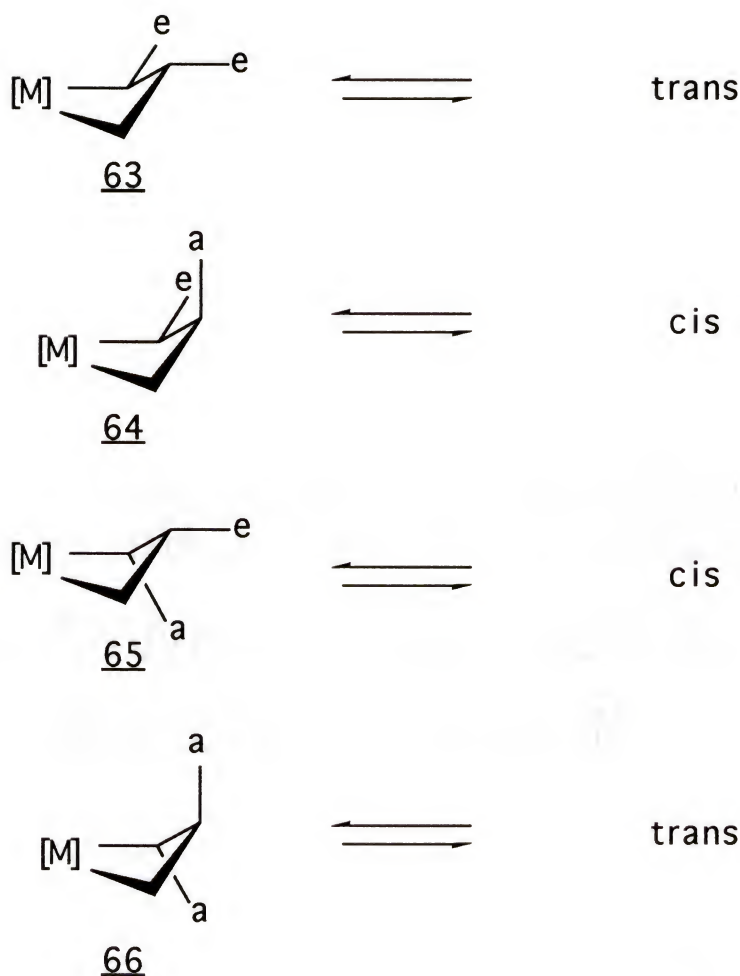


Figure 4-14. Puckered metallacycle model for determining stereoselectivity of the olefin metathesis reaction, where (a) represents axial, and (e) represents equatorial.¹¹²

This same model can be used to explain the high *cis* stereoselectivity observed in the metathesis of the α branched olefins. α branching increases the steric bulk of the metallacycle substituents, and it is conceivable that the steric bulk is increased to the point that the preferred α -equatorial, β -equatorial substitution pattern of metallacycle 63 becomes an unfavorable configuration as the substituents interact significantly

with each other. This interaction is relieved when one alkyl group occupies an equatorial position while the other group is axial. Since the alpha substituent prefers the equatorial position due to the strong interaction with the ligands of the metal center, metallacycles 65 and 66 are not favorable configurations. The beta carbon is farthest from the metal center and its ligands, so the beta substituent in the axial position becomes the preferred configuration, as in metallacycle 64. Therefore, the stereoselectivity favoring the cis isomer found in these reactions indicates that the interaction of the metallacycle substituents is increased with the alpha branching of the olefin, and that this interaction becomes more important in determining the stereochemistry of the product than the interaction between the beta axial substituent of the metallacycle with the catalyst ligands.

The same stereoselectivity is demonstrated by both the tungsten 15 and the molybdenum 16 catalysts, which indicates that these interactions are present in both catalyst structures. Assuming the only difference between the reaction of vinylcyclohexane 58 and 3-methylhexene 50 is a matter of degree and not kind, the metallacycle formed in the reaction of 3-methylhexene with the tungsten catalyst (Figure 4-4a) would have an alpha equatorial and a beta axial substitution pattern.

ADMET Polymerization of Alpha-Substituted Dienes

The alpha substituted olefin model study demonstrated that through proper choice of catalyst, alpha substituted olefins could be quantitatively metathesized. The explanations offered above are

consistent with the experimental results as well as the literature. The only conclusion that is of any consequence to ADMET polymerization chemistry is the tungsten catalyst 15 is not applicable to the ADMET polymerizations of alpha substituted olefins, whereas the activity demonstrated by the molybdenum catalyst 16 meets all of the criteria for successful ADMET polymerizations of alpha substituted olefins, and is the sole catalyst employed for the polymerizations reported below.

Polymerization of 3-methyl-1,5-hexadiene

3-Methyl-1,5-hexadiene 52 reacts with the tungsten catalyst 15 essentially as a monofunctional olefin, but with the molybdenum catalyst 16, this compound is a difunctional monomer that readily polymerizes to poly(3-methylbutenylene) 67. This polymer is an isomer of a well known and industrially important polymer, 1,4-polyisoprene (Figure 4-15).

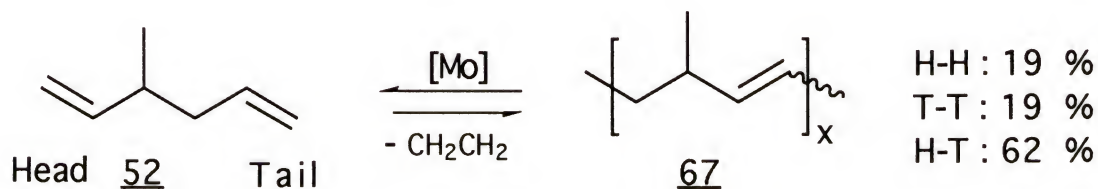


Figure 4-15. ADMET polymerization of 3-methyl-1,5-hexadiene 52, where H-H, T-T, and H-T represent the head-to-tail, tail-to-tail, and head-to-tail bonds, respectively. [Mo] represents catalyst 16.

The structure of poly(3-methylbutenylene) 67 is complicated by the relative positioning of the methyl group along the polymer backbone. Monomer 52 possesses a 'head' and a 'tail' since the

methyl group is alpha to one vinyl group and beta to the other. The convention adopted refers to the alpha substituted vinyl end as the 'head', while the beta substituted vinyl end is termed the 'tail'. Fortunately, the dimerized product of 52 provided the perfect model for the tail-to-tail olefin linkage in the polymer (Figure 4-6). The quantitative ^{13}C NMR of polymer 67 (Figure 4-16) shows the two sp^2 carbon signals that correspond to the tail-to-tail linkage at 128.6 ppm (cis) and 130.0 ppm (trans). Stoichiometry dictates that for every tail-to-tail linkage, there must be a corresponding head-to-head linkage, which appears at 134.2 ppm as one overlapping signal for both the cis and the trans isomers. As expected, the integration of the head-to-head signal equals the sum of the tail-to-tail resonances.

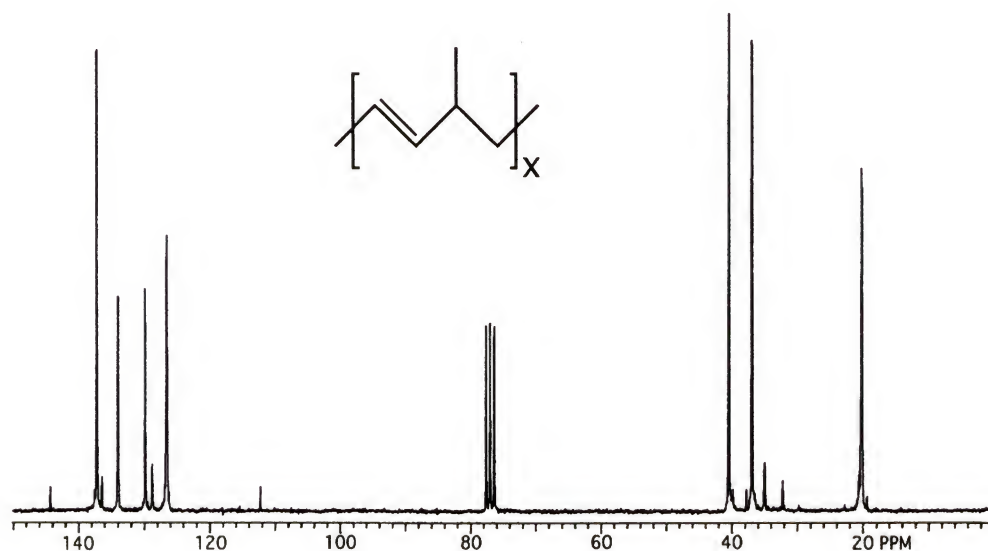


Figure 4-16. Quantitative ^{13}C NMR spectrum of poly(3-methylbutenylene) 67.

The head-to-tail bond provides four additional carbon signals, which appear as two sets of cis and trans isomers that must be equal in intensity. The carbons of the head-to-tail bond were assigned based upon their relative chemical shifts as compared to the relative chemical shifts of the head-to-head and tail-to-tail resonances. Since the carbon signal of the head-to-head linkage is further downfield than the signal for the tail-to-tail bond, the head carbon of the head-to-tail linkage was assigned to the signal further downfield, thus the carbon signals at 137.7 ppm and 136.8 ppm were designated the head carbon of the head-to-tail bond, corresponding to the trans and cis isomers, respectively. The tail carbon of the head-to-tail bond appears at 127.5 ppm as one signal for the two overlapping resonances of the cis and trans isomers. Again, the integrals of the two carbon signals that make up the same bond, in this case the head-to-tail olefin, are equal in value.

The endgroups of polymer 67 are also evident in the quantitative ^{13}C NMR spectrum. Of the two possible endgroups, only the alpha substituted vinyl group is detected (CH_2 112.3 ppm and CH 144.3 ppm), which indicates that the alpha substituted (head) vinyl group is less reactive than the beta substituted (tail) vinyl group.

The distribution of the various types of linkages in poly(2-methylbutenylene) 67 should be random if the two vinyl groups in the monomer are equal in reactivity. Analysis of the quantitative ^{13}C NMR spectra shows a relative distribution of 0.19/ 0.20/ 0.62 for the head-to-head/ tail-to-tail/ tail-to-head polymer linkages, respectively; the statistical distribution is 0.25/ 0.25/ 0.50 for the same bonds. There seems to be a slight preference for the formation

of the head-to-tail bond. The scenario that best describes the polymerization reaction has the tail vinyl groups, being the more reactive olefin, forming dimers faster than the head vinyl groups. This relative reactivity is supported by the lack of any 'tail' vinyl endgroups in the polymer 67. The transmetathesis of the tail-to-tail internal olefin with the head vinyl group is faster than the formation of the head-to-head linkage, therefore, the head-to-tail bonds form preferentially over the head-to-head bonds. However, given that the polymer consists almost entirely of internal olefins, the transmetathesis between internal olefins would eventually randomize the distribution of all the linkages in the polymer.

Another interesting point about this polymer is that the cis/trans ratio from one linkage to the other was found to be inconsistent; this ratio for the tail-to-tail bond is 8.7×10^{-2} (92 % trans), which is typical for an ADMET reaction of a linear diene. Therefore, the beta substitution exerts no influence on the stereochemistry of this bond. In contrast, the head-to-tail bond has a cis/trans ratio of 12 (7.8 % trans) thus the presence of only one alpha methyl group has a marked effect on the stereochemistry of the metathesized olefin. Unfortunately, the relative stereochemistry of the head-to-head bond is not discernible from the spectrum in Figure (4-16).

Polymerization of *cis*-1,2-divinylcyclohexane

Each of the two additional alpha substituted monomers polymerized with the molybdenum catalyst 16 contained an alpha cyclohexyl ring. The first was *cis*-1,2-divinylcyclohexane 68, which

produced a modest molecular weight polymer 69, $M_n = 7,800$ (SEC) (Figure 4-17). The *cis*/*trans* ratio follows the stereoselectivity trend established by the model olefin study with a value of 7.3 (88% *cis*). Polymer 69 is not unique since it has previously been synthesized by ring opening metathesis polymerization (ROMP) techniques employing bicyclo[4.2.0]-5-octene.¹¹³

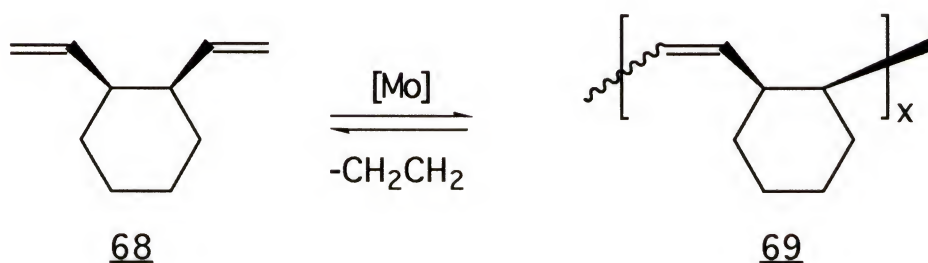


Figure 4-17. ADMET polymerization of *cis*-1,2-divinylcyclohexane 68 where [Mo] represents catalyst 16.

Polymerization of *trans*-1,4-divinylcyclohexane

The second cyclohexyl containing monomer polymerized in this study, *trans*-1,4-divinylcyclohexane 70, produces a polymer structure that is unobtainable by ROMP techniques, although the *cis* isomeric polymer has been synthesized by the ring opening metathesis polymerization of bicyclo[2.2.2]octene.¹¹⁴

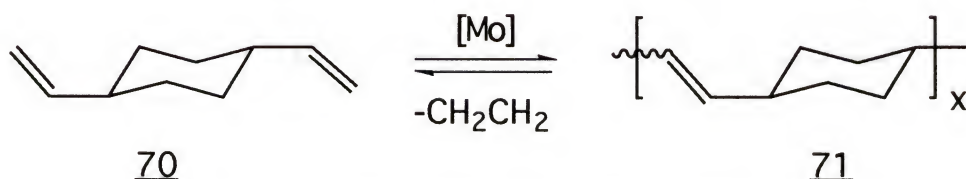


Figure 4-18. ADMET polymerization of *trans*-1,4-divinylcyclohexane 70 where [Mo] represents catalyst 16.

The product of the ADMET polymerization of *trans*-1,4-divinylcyclohexane 70 was a crystalline solid 71, which consisted of two fractions, the chloroform soluble and insoluble fractions. Integration of the vinyl signals relative to internal olefin signals in the ^1H NMR of the soluble fraction revealed that polymer 71 was on average, pentamer, and the insoluble fraction could not possess a much higher molecular weight. Dissolution brought about by the rigid structure of the repeat unit limits the molecular weight of the crystalline polymer 71, not the metathesis activity of the catalyst. The characterization data for all three alpha substituted dienes polymerizations performed with the molybdenum catalyst 16 is summarized in Table (4-2).

Table 4-2. α -Substituted Polymer Data Summary

Monomer	M_n (VPO) ^a ($\times 10^3$)	M_n (SEC) ^b ($\times 10^3$)	DSC Data ^c ($^{\circ}\text{C}$)	TGA Data ^d ($^{\circ}\text{C}$)
3-methyl-1,5-hexadiene <u>52</u>	5.8	6.1	Tg= -58	345
<i>cis</i> -1,2-divinylcyclohexane <u>68</u>	8.0	7.8	Tg= 22	266
<i>trans</i> -1,4-divinylcyclohexane <u>70</u>	----	1.0	Tm= 120	278
a) Vapor Pressure Osmometry, calibrated with sucrose octaacetate, (g/mol) b) Size Exclusion Chromatography, relative to polybutadiene standards (g/mol) c) Differential Scanning Calorimetry, scan rate 10 $^{\circ}\text{C}/\text{min}$ d) Thermal Gravimetric Analysis, heating rate 10 $^{\circ}\text{C}/\text{min}$, under nitrogen atm.				

Summary

The synthesis of the polymers mentioned above establishes alpha branched hydrocarbons as monomers in ADMET polymerization chemistry, which was predicted by the results of the model compound study. Some of the differences in reactivity between the

tungsten 15 and molybdenum 16 based catalysts have also been defined, with the key to the successful polymerization of alpha substituted hydrocarbon monomers being the proper choice of catalyst; of the two catalysts that have been successfully applied to ADMET polymerizations, only the molybdenum catalyst will polymerize alpha branched dienes. The results of this investigation can now be utilized in the design of monomers for future ADMET polymerizations.

CHAPTER 5

EXPERIMENTAL

Instrumentation

Proton nuclear magnetic resonance (NMR) (200 MHz) and ^{13}C NMR (50 MHz) spectra were obtained on a Varian XL-200 Series NMR Superconducting Spectrometer. Chemical shifts are reported in parts per million down field from tetramethylsilane (TMS). Spectra were obtained in CDCl_3 with 1% TMS unless otherwise noted. Ultraviolet spectra were collected on a Perkin-Elmer Lambda 9 UV/Vis/NIR spectrometer with pentane as solvent. Infrared spectroscopy was performed on a Perkin-Elmer F9 FTIR spectrophotometer; samples were run neat when possible, otherwise a nujol mull of the sample was prepared. Low resolution gas chromatography was performed on a HP 5880A gas chromatograph. Mass spectroscopy was performed on a Finnigan 4500 Gas Chromatograph / Mass Spectrometer. Elemental analyses of compounds were performed by Atlantic Microlab Inc. in Norcross, Georgia.

Differential scanning calorimetry (DSC) data was collected on a Du Pont DSC 2910 Differential Scanning Calorimeter with nitrogen purge gas at a heating rate of 10°C per minute. The thermal gravimetric analysis (TGA) of the polymers were carried out on a

DuPont Hi-Res TGA 2950 Thermogravimetric Analyzer , under a flow of dry nitrogen at a heating rate of 10°C per minute. Size exclusion chromatography (SEC) was carried out with the use of Phenomenex Phenogel 5,500 Å and 5,000 Å columns coupled together, a Waters Associates differential refractometer, and a Perkin-Elmer LC-75 spectrophotometric detector on polymer samples 0.5% (w/v) in THF. The instrument was relatively calibrated with 1,4-polybutadiene standards obtained from Polysciences, Inc. ranging from $M_n=900$ to $M_n= 22,000$. Vapor pressure osmometry (VPO) data was obtained, for polymer samples ranging from 10 to 30 g/L in toluene, on a Wescam Vapor Pressure Osmometer model 233 at 50°C. Intrinsic viscosities were determined with an Oswaldt dilution viscometer at 25°C in toluene.

Catalysts

Three varieties of a Lewis acid free metathesis catalyst, $M(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{Pr}_2)[\text{OCCH}_3\text{CF}_3]_2]_2$, where M = tungsten and molybdenum, and R= Me and Phenyl, were prepared according to literature methods.^{84,93} Catalyst was stored dry under an inert atmosphere.

Purification of Reagents and Solvents

The sensitivity of these catalysts to water and oxygen, as well as the requirements of purity dictated by the step condensation nature of the polymerization reaction, required that all reagents be of the utmost purity, with the exclusion of both oxygen and water being crucial.⁵⁹ The general procedure followed for all volatile reagents was to stir over calcium hydride in a round bottom flask

stoppered with a drying tube filled with drierite® for 48 hrs or until evolution of hydrogen gas was no longer evident. The pre-dried reagent was then attached to a high vacuum line and degassed a minimum of four times via freeze pump thaw cycles. This compound was then stirred for 24 hrs with intermittent degassing, the frequency depending on hydrogen evolution. When the reagent appeared dry, it was transferred under vacuum to a potassium mirrored flask and stirred for 24 hrs; additional mirrored flasks were utilized when necessary. When dry, the reagent was transferred into a storage flask that could be sealed and removed from the vacuum line.

Solid reagents were sublimed under reduced pressure and stored under argon in a dry-box, while non-volatile oils were heated under high vacuum (10^{-6}) for 48 hrs.

Toluene was purified by shaking with a dilute basic solution of KMnO_4 in water, followed by water and then concentrated sulfuric acid until the acid layer remained clear. The toluene was then washed with water, dried over magnesium sulfate and distilled from calcium hydride. Finally, this pre-dried toluene was distilled from a sodium potassium amalgam.¹¹⁵ Deuterated benzene was purchased from Aldrich Chemical Co., gold label, opened under inert atmosphere and stored over 4 Å sieves. Tetrahydrofuran was distilled from potassium benzophenone ketyl.

General ADMET Reaction Conditions

The reaction conditions employed for all polymerizations and model studies are the optimum conditions previously described.⁵⁹

All reactions were performed on a high vacuum line to ensure dryness. All glassware was flame dried under vacuum. Only pure, dry reagents were used. The application of an intermittent vacuum was employed to remove any condensate. The reactions were not heated above 50°C to avoid decomposition of the catalyst. Reaction flasks were equipped with a gas trap and a dry ice-isopropanol condenser so that ethylene could be removed from the reaction without the loss of reactant.

NMR Solution Reactions

In order to gain further insight into the reactions that showed no metathetic activity, solution reactions were performed in d_6 -benzene and monitored via ^1H NMR. Typically, 25 mg of the catalyst, $\text{M}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where $\text{R} = \text{Phenyl}$, and M was either tungsten or molybdenum, were dissolved in 500 μL of d_6 -benzene in an inert atmosphere. This solution was added to an NMR tube equipped with a young valve. Ten microliters of the alkene were then directly syringed into the tube and the valve closed. The reaction was then monitored by ^1H NMR immediately, and followed for the course of the reaction.

Copolymerization of 1,5-Hexadiene (3) and 1,9-Decadiene (5)

Monomers, 1,5-hexadiene and 1,9-decadiene, were purchased from Aldrich Chemical Co. in the highest purity available. The 1,9-decadiene was 99+ % pure and only needed to be dried before use. The 1,5-hexadiene was only available as 98 % and was fractionally distilled twice prior to drying.

Synthesis of poly(1,4-butadiene-co-octenamer) 50:50 ratio (17)

In an argon filled dry box, 1.22 mL of 1,9-decadiene (6.62 mmol) were syringed into a dried breakseal fitted with a glass constriction and a rotoflow™ valve. To this same breakseal, 0.78 mL of 1,5-hexadiene (6.34 mmol) was added and the container sealed by closing the rotoflow™ valve. The breakseal was then removed from the dry box and attached to the vacuum line where it was degassed via freeze pump thaw cycles. Once thoroughly degassed, the monomer feed was frozen in liquid nitrogen and the glass constriction sealed under vacuum. A breakseal of catalyst was prepared by adding a solution containing 20 mg of $W(CHCMe_2R)(N-2,6-C_6H_3-i-Pr_2)[OCCH_3(CF_3)_2]_2$, where $R = Me$ 15, in one mL of pentane. This breakseal was carried through the same degassing procedures as the other and sealed under vacuum. Both breakseals were attached to the reaction flask equipped with hammers to break open the breakseals. This flask was attached to the vacuum line and flamed dried under high vacuum. The catalyst solution was introduced to the flask first, and the pentane removed in vacuo. The monomer feed was then added to the dry catalyst. Ethylene was removed periodically, by collection into the liquid nitrogen trap and subsequently released into the vacuum line. All monomer condensed in the gas trap was transferred back onto the catalyst. The reaction was heated to 50°C and stirred via magnetic agitation. The reaction was terminated by exposure to the atmosphere when stirring ceased.

The polymer produced was dissolved in toluene and passed through a column of alumina. After removal of the toluene, the

polymer was freeze dried from chloroform. Yielding 0.99 grams of a white copolymer that had the following spectral properties:

Yield: 94 %

^1H NMR: 1.30 (br, 2H); 2.05 (br, 4H); 5.38 (br, 2H)

^{13}C NMR: 27.8, 29.6, 29.9, 32.4, 129.1, 129.7, 129.9, 130.0, 130.2, 130.3, 130.7

IR (neat, cm^{-1}): 2917.5, 1776.2, 1666.6, 1640.9, 956.4

Elemental Analysis: Calculated for C_6H_{10} : C, 87.80%; H, 12.20%
Found: C, 86.92%; H, 12.80%.

SEC (gm/mol): $M_w = 15,000$ PDI= 1.93

VPO (gm/mol): $M_n = 7980$

$[\eta]$ (g/dL): 0.30 TGA (onset): 436°C

Synthesis of poly(1,4-butadiene-co-octenamer) 25:75 ratio (18)

For this synthesis, the same procedures used for the 50:50 copolymerization were followed with 1.65 mL of 1,9-decadiene (8.95 mmol) and 0.35 mL of 1,5-hexadiene (2.95 mmol) making up the monomer feed.

The polymer produced was dissolved in toluene and passed through a column of alumina. After removal of the toluene, the polymer was freeze dried from chloroform. Yielding 1.1 grams of a white copolymer that had the following spectral properties:

Yield: 98 %

^1H NMR: 1.30 (br, 3H); 2.05 (br, 4H); 5.38 (br, 2H)

^{13}C NMR: 27.8, 29.6, 29.9, 32.4, 129.1, 129.7, 129.9, 130.0, 130.2, 130.3, 130.7

IR (neat, cm^{-1}): 2914.6, 1775.7, 1664.8, 1641.4, 955.5

Elemental Analysis: Calculated for C_7H_{12} : C, 87.50%; H, 12.50%

Found: C, 87.43%; 12.32%.

SEC (gm/mol): M_w = 25,200 PDI = 1.98

VPO (gm/mol): M_n = 12,400

$[\eta]$ (g/dL): 0.35

TGA (onset): 438°C

Synthesis of poly(1,4-butadiene-co-octenamer) 10:90 ratio (19)

For this synthesis, the same procedures used for the 50:50 copolymerization were followed with 1.87 mL of 1,9-decadiene (10.1 mmol) and 130 μ L of 1,5-hexadiene (1.1 mmol) making up the monomer feed.

The polymer produced was dissolved in toluene and passed through a column of alumina. After removal of the toluene, the polymer was freeze dried from chloroform. Yielding 1.1 grams of a white copolymer that had the following spectral properties:

Yield: 91 %

1H NMR: 1.30 (br, 3.6H); 2.05 (br, 4H); 5.38 (br, 2H)

^{13}C NMR: 27.8, 29.6, 29.9, 32.4, 129.1, 129.7, 129.9, 130.0,
130.2, 130.3, 130.7

IR (neat, cm^{-1}): 2915.4, 1775.2, 1665.2, 1641.7, 956.2

Elemental Analysis: Calculated for $C_{7.8}H_{13.6}$: C, 87.30%; H, 12.70%

Found: C, 87.02%; H, 12.65%.

SEC (gm/mol): M_w = 15,000 PDI = 1.94

VPO (gm/mol): M_n = 7,960

$[\eta]$ (g/dL): 0.28

TGA (onset): 445°C

Synthesis of poly(1,4-butadiene-co-octenamer) 75:25 ratio (20)

For this synthesis, the same procedures used for the 50:50 copolymerization were followed with 0.68 mL of 1,9-decadiene (3.7 mmol) and 1.32 mL of 1,5-hexadiene (11.1 mmol) making up the monomer feed.

The polymer produced was dissolved in toluene and passed through a column of alumina. After removal of the toluene, the polymer was freeze dried from chloroform. Yielding 0.94 grams of a white copolymer that had the following spectral properties:

Yield: 93%

^1H NMR: 1.30 (br, 1H); 2.05 (br, 4H); 5.38 (br, 2H)

^{13}C NMR: 27.8, 29.6, 29.9, 32.4, 129.1, 129.7, 129.9, 130.0, 130.2, 130.3, 130.7

IR(neat, cm^{-1}): 2918.4, 1775.6, 1666.4, 1641.2, 962.7

Elemental Analysis: Calculated for C_5H_8 : C, 88.20%; H, 11.80%
Found C, 87.45%; H, 12.09%

SEC (gm/mol): M_w = 18,200 PDI = 1.89

VPO (gm/mol): M_n = 9,820

TGA (onset): 432°C

Transmetathesis synthesis of poly(1,4-butadiene-co-octenamer) (17a)

For this synthesis, the same procedures used for the 50:50 copolymerization were followed with 1.2 mL of 1,9-decadiene (6.6 mmol) making up the initial monomer feed. Once polyoctenamer was formed, 0.78 mL of 1,5-hexadiene (6.6 mmol) was vacuum

transferred onto the solid polymer, and the reaction allowed to continued until the solution was again solid.

The polymer produced was dissolved in toluene and passed through a column of alumina. After removal of the toluene, the polymer was freeze dried from chloroform. Yielding 0.92 grams of a white copolymer that had the following spectral properties:

Yield: 85%

^1H NMR: 1.30 (br, 2H); 2.05 (br, 4H); 5.38 (br, 2H)

^{13}C NMR: 27.8, 29.6, 29.9, 32.4, 129.1, 129.7, 129.9, 130.0, 130.2, 130.3, 130.7

IR(neat, cm^{-1}): 2918.3, 1776.6, 1665.8, 1641.3, 958.4

Elemental Analysis: Calculated for C_7H_{12} : C, 87.50%; H, 12.50%

Found: C, 87.01%; H, 12.79%

SEC (gm/mol): M_w = 15,200 PDI = 1.90

VPO (gm/mol): M_n = 7,940

TGA (onset): 441°C

Transmetathesis synthesis of poly(1,4-butadiene-co-octenamer) (17b)

For this synthesis, the same procedures used for the transmetathesis of polyoctenamer were followed with 0.78 mL of 1,5-hexadiene (6.6 mmol) making up the initial monomer feed. Once 1,4-polybutadiene was formed, 1.22 mL of 1,9-decadiene (6.6 mmol) was vacuum transferred onto the solid polymer, and the reaction allowed to continued until the solution was again solid.

The polymer produced was dissolved in toluene and passed through a column of alumina. After removal of the toluene, the

polymer was freeze dried from chloroform. Yielding 0.88 grams of a white copolymer that had the following spectral properties:

Yield: 89%

^1H NMR: 1.30 (br, 2H); 2.05 (br, 4H); 5.38 (br, 2H)

^{13}C NMR: 27.8, 29.6, 29.9, 32.4, 129.1, 129.7, 129.9, 130.0, 130.2, 130.3, 130.7

IR(neat, cm^{-1}): 2919.2, 1775.8, 1665.4, 1640.2, 955.7

Elemental Analysis: Calculated for C_7H_{12} : C, 87.50%; H, 12.50%

Found: C, 87.33%; H, 12.67%

SEC (gm/mol): M_w = 14,800 PDI = 1.96

VPO (gm/mol): M_n = 7,580

TGA (onset): 433°C

Block Copolymerization of 1,9-Decadiene and 1,5-Hexadiene

Reaction 1 - synthesis of (21).

In an argon filled dry box, 1.22 mL of 1,9-decadiene (6.6 mmol) were measured into an 50 mL roundbottom flask possessing a rotoflow™ valve. To this flask, 20 mg of $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were added directly. Instantly the reaction began to foam. The reaction was removed from the dry box and attached to the vacuum line, where the ethylene was removed. Once the solution had become solid, 0.78 mL (6.6 mmol) of 1,5-hexadiene were vacuum transferred onto the solid polyoctenamer. When no reaction was evident, the flask was taken back into the dry box and another 20 mg of catalyst added. Again the reaction began to foam, so the flask was returned to the vacuum line

where the ethylene was removed. When the solution was again solid, the reaction was terminated by exposure to the atmosphere.

The polymer produced was dissolved in toluene and passed through a column of alumina. After removal of the toluene, the polymer was freeze dried from chloroform. Yielding 0.90 grams of a white copolymer that had the following spectral properties:

Yield: 91%

^1H NMR: 1.30 (br, 2H); 2.05 (br, 4H); 5.38 (br, 2H)

^{13}C NMR: 27.8, 29.6, 29.9, 32.4, 129.1, 129.7, 129.9, 130.0, 130.2, 130.3, 130.7

IR(neat, cm^{-1}): 2916.9, 1777.5, 1667.8, 1641.3, 958.3

Elemental Analysis: Calculated for C_7H_{12} : C, 87.50%; H, 12.50%

Found: C, 87.02%; H, 12.72%

SEC (gm/mol): $M_w = 14,600$ PDI = 2.11

TGA (onset): 438°C

Reaction 2 - synthesis of (22).

This reaction is analogous to reaction 1 described above, with one exception; the SEC (gm/mol)ond monomer, 1,5-hexadiene, was syringed into the reaction flask in the argon filled dry box. Since the reaction foamed upon addition, the SEC (gm/mol)ond addition of catalyst was not added.

The polymer produced was dissolved in toluene and passed through a column of alumina. After removal of the toluene, the polymer was freeze dried from chloroform. Yielding 0.92 grams of a white copolymer that had the following spectral properties:

Yield: 93%

^1H NMR: 1.30 (br, 2H); 2.05 (br, 4H); 5.38 (br, 2H)
 ^{13}C NMR: 27.8, 29.6, 29.9, 32.4, 129.1, 129.7, 129.9, 130.0, 130.2, 130.3, 130.7
 IR(neat, cm^{-1}): 2917.2, 1776.5, 1666.6, 1640.3, 956.6
 Elemental Analysis: Calculated for C_7H_{12} : C, 87.50%; H, 12.50%
 Found: C, 86.90%; H, 12.85%
 SEC (gm/mol): M_w = 12,200 PDI= 1.98
 VPO (gm/mol): M_n = 6,370
 TGA (onset): 436°C

The Metathesis Activity of 1,1-Disubstituted
and Trisubstituted Olefins

Attempted metathesis of 2,5-dimethyl-1,5-hexadiene (24) with
the tungsten catalyst (15)

This compound was purchased from Aldrich Chemical Co. as 99% pure and dried as described above. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{W}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

Attempted metathesis of 2,5-dimethyl-1,5-hexadiene (24) with
the molybdenum catalyst (16)

This compound was purchased from Aldrich Chemical Co. as 99% pure and dried as described above. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{Pr}_2)$

$[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

Synthesis of 2,9-dimethyl-1,5,9-decatriene (28) with the tungsten catalyst (15)

The diene 27 was purchased from Aldrich Chemical Co. as 99% pure and dried as described above. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{W}(\text{CHCMe}_2\text{R})(\text{N}-2,6-\text{C}_6\text{H}_3-i\text{Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis. The clear liquid consisted entirely of the dimer, 2,9-dimethyl-1,5,9-decatriene 28.

Yield: 94 %

^1H NMR: 1.72(s, 6H); 2.11(br, m, 8H); 4.73(br, d, 4H); 5.42(br, m, 2H)

^{13}C NMR: 22.2, 25.8, 30.8, 37.9, 110.0, 129.9, 130.1, 145.9

IR(neat, cm^{-1}): 2930.4, 1779.4, 1649.4, 1447.0, 966.4

Elemental Analysis: Calculated for $\text{C}_{12}\text{H}_{20}$: C, 87.80%; H, 12.20%.
Found: C, 87.43%; H, 12.31%.

Synthesis of polyisoprene (29) with the molybdenum catalyst (16)

The monomer 27 was purchased from Aldrich Chemical Co. as 99% pure and dried as already described. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N}-2,6-\text{C}_6\text{H}_3-i\text{Pr}_2)$

$[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. The reaction was allowed to continue until stirring via magnetic agitation became impossible. The resulting polymer was dissolved in toluene and passed through a column of alumina, followed by freeze drying from chloroform. The clear polymer had the following spectral properties:

Yield: 92 %

^1H NMR: 1.65(d, 3H); 2.05(br, 4H); 5.15(br, m, 2H)

^{13}C NMR: 16.1, 22.4, 23.6, 26.4, 32.2, 32.3, 38.0, 38.1, 39.8, 40.1, 110.2, 124.2, 125.3, 134.8 (multiple signals), 145.8

SEC (gm/mol): M_w = 9,400 PDI= 1.97

VPO (gm/mol): M_n = 4,920

Elemental Analysis: Calculated for C_5H_8 : C, 88.34%; H, 11.76%.

Found: C, 88.01%; H, 11.85%.

IR(neat, cm^{-1}): 2992.3, 1665.3, 1447.4, 1376.6

TGA(onset): 364°C

DSC: T_g = -72°C

Synthesis of 1,4-diisopropenylbenzene (31)

This compound was synthesized according to literature methods.¹¹⁶ The reaction was carried out using standard schlenk line techniques with argon as the inert gas. In a 500 mL round bottom flask, 300 mL of dry diethyl ether was added to 20 mL of 1,4-dichlorobenzene (Aldrich) (178 mmoles) and $[\text{Ni}(\text{dmpe})\text{Cl}_2]$ (Aldrich) (0.8 mmoles) was added. To this solution, a previously prepared slurry of isopropenylmagnesium bromide (Aldrich) in

diethyl ether, 500 mmol, was added dropwise. After the reaction mixture was refluxed for 24 hrs, the reaction was quenched with dilute HCl. The ether layer was then washed with portions of water and NaHCO₃, and subsequently dried over MgSO₄. The ether was removed and the resulting solid sublimed three times at 50°C under reduced pressure (10⁻³ mmHg). The final product, a white crystalline material, had the following spectral properties:

Yield: 65 %

¹H NMR: 2.14(s, 6H); 5.06(m, 2H); 5.38(m, 2H); 7.41(s, 4H)

¹³C NMR: 21.9, 112.2, 125.8, 140.0, 143.2

Elemental Analysis: Calculated for C₁₂H₁₄: C, 91.14%; H, 8.86%.

Found: C, 91.10%; H, 8.83%.

Attempted metathesis of 1,4-diisopropenylbenzene (31) with the tungsten catalyst (15)

1,4-Diisopropenylbenzene 31 was synthesized and dried as described above. This reaction was performed in a 50 mL roundbottom flask with a rotoflow™ valve attached. In an argon filled dry box, 1.0 gram of 1,4-diisopropenylbenzene was dissolved in a minimal amount of dry toluene in the reaction flask. Once dissolved, 20 mg of catalyst W(CHCMe₂R)(N-2,6-C₆H₃-*i*-Pr₂) [OCCH₃(CF₃)₂]₂, where R= Phenyl, were added directly. The reaction flask was sealed and removed from the dry box and attached to the high vacuum line. The reaction was stirred for 24 hrs at room temperature with intermittent vacuum applied on an hourly basis for 10 hrs. The reaction was heated to 50°C for the next 48 hrs, again, intermittent vacuum was applied on an hourly basis for ten hours per

day. After the allotted 72 hour reaction time, the toluene was stripped off and the contents of the flask analyzed.

Attempted metathesis of 1,4-diisopropenylbenzene (31) with the molybdenum catalyst (16)

1,4-Diisopropenylbenzene 31 was synthesized and dried as described above. This reaction was performed analogously to the reaction of 1,4-diisopropenylbenzene with the tungsten catalyst. Twenty milligrams of catalyst $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were added directly. After the 72 hour reaction time, the toluene was stripped off and the contents of the flask were analyzed.

The disproportionation of 2-methyl-2-butene (32) with the tungsten catalyst (15)

Compound 32 was purchased from Aldrich Chemical Co. as 99% pure and was dried as previously described. In an argon filled dry box, 2.0 mL of this reactant was syringed into a 50 mL roundbottom flask equipped with a rotoflow™ valve. The catalyst, 20 mg of $\text{W}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, was then dissolved in the liquid reactant, and the rotoflow™ closed. The reaction flask remained sealed for the entire reaction period of one week; at that time, the side arm of the flask was stoppered with a suba seal septum. The rotoflow was then opened and a sample removed for analysis via high resolution GC/MS.

GC/MS: 1st peak (2-butene): M^+ , 56.0664; $\text{M}(100)$ 41.0452

2nd peak (2-methyl-2-butene): M^+ , 70.0688; $\text{M}(100)$ 55.0582

3rd peak(2,3-dimethyl-2-butene): M⁺, 84.0946; M(100)
69.0644

The disproportionation of 2-methyl-2-butene (32) with the molybdenum catalyst (16)

Compound 32 was purchased from Aldrich Chemical Co. as 99% pure and was dried as previously described. In an argon filled dry box, 2.0 mL of this reactant was syringed into a 50 mL roundbottom flask equipped with a rotoflow™ valve. The catalyst, 20 mg of Mo(CHCMe₂R)(N-2,6-C₆H₃-*i*Pr₂)[OCCH₃(CF₃)₂]₂, where R= Phenyl, was then dissolved in the liquid reactant, and the rotoflow™ closed. The reaction flask was not heated and remained sealed for the entire reaction period of one week; at that time, the side arm of the flask was stoppered with a suba seal septum. The rotoflow was then opened and a sample removed for analysis via high resolution GC/MS.

GC/MS: 1st peak (2-butene): M⁺, 56.0587; M(100) 41.0672

2nd peak (2-methyl-2-butene): M⁺, 70.0363; M(100) 55.0495

3rd peak(2,3-dimethyl-2-butene): M⁺, 84.0642; M(100) 69.0468

Synthesis of 3,6-dimethyl-2,6-octadiene (35)

Compound 35 was synthesized via the Wittig reaction,¹¹⁷ following a procedure analogous to that used for the synthesis of propenylcyclohexane. Acetylacetone, 11.7 mL (100 mmol) in 25 mL of THF were added dropwise to a stirring, cold(-78°C) solution of ethyltriphenylphosphonium bromide ylid (200 mmol) in THF, allowed to warm, then refluxed overnight. The same isolation procedure was followed as above, 13.6 grams of the expected product were isolated by vacuum transferring the liquid from the salts.

Yield: 99%

^1H NMR: 1.58(m, 3H); 1.65(m, 3H); 2.08(m, 2H); 5.18(m, 1H)

^{13}C NMR: 13.1, 13.2, 23.8, 29.8, 30.2, 37.9, 38.3, 118.1, 118.9, 136.0, 136.2

GC/MS: M^+ , 138.1405; $\text{M}(100)$, 123.1441

Elemental Analysis: Calculated for $\text{C}_{10}\text{H}_{18}$: C, 86.96%; H, 13.04%
 Found: C, 86.85%; H, 13.10%.

Attempted metathesis of 3,6-dimethyl-2,6-octadiene (35) with the tungsten catalyst (15)

Compound 35 was synthesized and dried as described previously. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{W}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

Attempted metathesis of 3,6-dimethyl-2,6-octadiene (35) with the molybdenum catalyst (16)

Compound 35 was synthesized and dried as described previously. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

Attempted metathesis of squalene (36) with the tungsten catalyst (15).

Compound 36 was purchased from Aldrich Chemical Co. as 99% pure and was dried by heating at 100°C under static high vacuum for 24 hrs. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $W(CHCMe_2R)(N-2,6-C_6H_3-iPr_2)[OCCH_3(CF_3)_2]_2$, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, the flask was opened to the atmosphere and the contents analyzed.

Attempted metathesis of squalene (36) with the molybdenum catalyst (16)

Compound 36 was purchased from Aldrich Chemical Co. as 99% pure and was dried by heating at 100°C under static high vacuum for 24 hrs. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $Mo(CHCMe_2R)(N-2,6-C_6H_3-iPr_2)[OCCH_3(CF_3)_2]_2$, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, the flask was opened to the atmosphere and the contents analyzed.

Attempted metathesis of methylenecyclohexane (37) with the tungsten catalyst (15)

Compound 37 was purchased from Aldrich Chemical Co. as 99% pure and was dried as described previously. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $W(CHCMe_2R)(N-2,6-C_6H_3-iPr_2)$

$[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

Attempted metathesis of methylenecyclohexane (37) with the molybdenum catalyst (16)

Compound 37 was purchased from Aldrich Chemical Co. as 99% pure and was dried as described previously. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

Attempted metathesis of ethylenecyclohexane (38) with the tungsten catalyst (15)

Compound 38 was purchased from Aldrich Chemical Co. as 99% pure and was dried as described previously. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{W}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

Attempted metathesis of ethylenecyclohexane (38) with the molybdenum catalyst (16)

Compound 38 was purchased from Aldrich Chemical Co. as 99% pure and was dried as described previously. The reaction flask was

prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R = Phenyl, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

Alternating Copolymer Synthesis

Synthesis of 5-methyl-1,5,9-decatriene (43)

The procedure for the synthesis of 43 was directly analogous to that used to produce propenylcyclohexane. Twenty milliliters of 5-hexene-2-one (Aldrich) (173 mmol) were added to an ylid prepared from 72 grams (175 mmol) of 1-pentenyl-triphenylphosphonium bromide and 87.5 mL of a 2.0 molar solution of n-butyllithium in pentane. The isolated product was distilled at 78°C at 15 mm Hg.¹¹⁸

Yield: 45 %

^1H NMR: 1.60(s, 1.2H); 1.69(s, 1.8H); 2.12(m, 8H); 4.95(m, 4H); 5.18(br, 1H); 5.82(m, 2H).

^{13}C NMR: 16.0, 23.4, 27.3, 27.4, 31.4, 32.3, 32.4, 34.0, 34.2, 39.1, 114.3, 114.5, 124.1, 124.9, 134.8, 134.9, 138.8.

Elemental Analysis: Calculated for $\text{C}_{11}\text{H}_{18}$: C, 88.00%; H, 12.00%.

Found: C, 87.35%; H, 12.32%.

Synthesis of poly(5-methyl-1,5,9-decatriene) (44)

The monomer was synthesized and dried as previously described. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of catalyst, $\text{W}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R =

Phenyl, were used for this reaction. The reaction was allowed to continue until the contents could no longer be stirred by magnetic agitation; at this time, the flask was opened to the atmosphere and the polymer dissolved in toluene and passed through an alumina column., followed by freeze drying from chloroform. The resulting clear polymer had the following spectral properties:

Yield: 89 %

^1H NMR: 1.60(s, 1.2H); 1.72(s, 1.8H); 2.05(br, 8H); 5.13(br, 1H); 5.42(br, 2H).

^{13}C NMR: 16.0, 23.8, 26.0-34.0(multiple signals); 39.8, 124.0-126.0(multiple signals), 129-131(multiple signals), 35.5(multiple signals).

IR(neat, cm^{-1}): 2917.8, 2846.9, 1665.9, 1447.3, 965.6

Elemental Analysis: Calculated for C_9H_{14} : C, 88.52%; H, 11.48%.

Found: C, 88.04%; H, 11.67%.

GPC: M_w = 26,000 PDI = 1.98

VPO (gm/mol): M_n = 12,980

TGA(onset): 378°C

DSC: T_g = -58°C

Synthesis of 5,6-dimethyl-1,5,9-decatriene (45)

This monomer was synthesized utilizing McMurry carbonyl coupling chemistry.^{119,120} The $\text{TiCl}_3(\text{DME})_{1.5}$ reagent was prepared by refluxing DME (350 mL) in the presence of TiCl_3 (25 gm, 162 mmol) for 48 hrs under argon. The light blue precipitate was collected by filtration under argon followed by washing with dry pentane; the dry powder was stored in an argon atmosphere (32.0 gm,

80%). The Zinc-copper couple catalyst was prepared by the addition of CuSO₄ (0.75 gm, 4.7 mmol) to a suspension of zinc dust (9.8 gm, 150 mmol) in nitrogen purged water. This solid was washed with acetone, and ether, and dried and stored in an argon atmosphere.

The TiCl₃(DME)_{1.5} (21.0 gm, 86 mmol) reagent and ZnCu (20 gm) catalyst were weighed out and mixed dry in the reaction flask under argon. One half of one liter of DME was added to this mixture, followed by refluxing for two hours. Then, 2.0 mL (17.25 mmol) of 5-hexene-2-one (Aldrich) in 10 mL of DME was added dropwise and the reaction refluxed overnight. After cooling to room temperature, the reaction was diluted with 300 mL of pentane, filtered through a pad of Florosil™, and concentrated via rotoryevaporation to yield the crude product. This product was distilled at 80°C at 15 mm Hg.

Yield: 95 %

¹H NMR: 1.65(s, 3H); 2.13(m, 4H); 5.02(m, 2H); 5.85(m, 1H)

¹³C NMR: 18.0, 18.2, 32.4, 32.8, 33.8, 34.1, 114.1, 128.0, 128.2, 139.2.

Elemental Analysis: Calculated for C₁₂H₂₀: C, 87.80%; H, 12.20%.

Found: C, 87.33%; H, 12.48%.

Synthesis of poly(5,6-dimethyl-1,5,9-decatriene) (46)

The monomer 45 was synthesized and dried as previously described. This reaction is analogous to the polymerization of 5-methyl-1,5,9-decatriene. Twenty milligrams of catalyst, W(CHCMe₂R)(N-2,6-C₆H₃-*i*Pr₂)[OCCH₃(CF₃)₂]₂, where R= Phenyl, were added directly to the reaction flask that contained 2.0 gm of the monomer. The reaction was terminated via exposure to the

atmosphere. The contents of the flask were dissolved in toluene and passed through a column of alumina, followed by freeze drying from chloroform. The clear polymer had the following spectral properties:

Yield: 93 %

^1H NMR: 1.69(m, 3H); 2.17(br, 4H); 5.34(0.24H); 5.42(0.76H)

^{13}C NMR: 18.0, 18.2, 26.0, 26.5, 29.3, 29.8, 31.5, 32.0, 34.6, 35.0, 128.1, 128.4, 129.7, 130.4.

Elemental Analysis: Calculated for $\text{C}_{10}\text{H}_{16}$: C, 88.24%; H, 11.76%.

Found: C, 87.90%; H, 11.32%.

SEC (gm/mol): M_w = 22,100 PDI= 1.93

VPO (gm/mol): M_n = 11,420

TGA(onset): 365°C

DSC: T_g = -53°C

Synthesis of 5,6-diphenyl-1,5,9-decatriene (47)

The method used to synthesize 47 is analogous to the procedure used for 5,6-dimethyl-1,5,9-decatriene. The ketone, 4-pentene-1-phenyl-1-one, used in this coupling was synthesized according to literature procedures.¹²¹ Acetophenone N,N-dimethylhydrazone was obtained by mixing acetophenone (2 gm, 200 mmoles) with N,N-dimethylhydrazine (20 mL, 250 mmol) and p-toluenesulphonic acid (0.25 gm) in 200 mL of benzene and refluxing for 2 hr. with removal of water by means of a Dean-Stark trap. The solution was neutralized with dilute KOH, washed with water, and dried over MgSO_4 . After filtration, the solvent was removed through rotoryevaporation, leaving behind acetophenone N,N

dimethylhydrazone. Acetophenone N,N dimethylhydrazone (24.0 gm, 150 mmol) was dissolved in 300 mL of dry THF under argon. Lithium diisopropylamide (150 mmol) was added at -78°C , followed by allylbromide (21.5 mL, 250 mmol). The reaction was warmed slowly to room temperature overnight, then poured into a pentane water mixture. The organic layer was extracted with brine, water, and dried over MgSO_4 . The solvent was removed by rotary evaporation, leaving a yellow liquid. 1-Phenyl-4-penten-one-N,N-dimethylhydrazone was isolated after distillation at 75°C at 0.5 mmHg. Concentrated HCl was added dropwise to a solution of 1-phenyl-4-penten-one-N,N-dimethylhydrazone in 100 mL of pentane, and the solution stirred for one hour. The reaction was diluted with water and the product extracted with pentane, washed with water and dried over MgSO_4 . The crude product was isolated after filtration by removal of the pentane. 1-Phenyl-4-penten-one was distilled at 62°C at 0.1 mm Hg.

5,6-Diphenyl-1,5,9-decatriene was synthesized by titanium coupling of 1-phenyl-4-penten-one, (2.0 gm) yielding 1.6 gm of product after distillation at 98°C at 10 mm Hg.

Yield: 89 %

^1H NMR: 2.12(m, 2H); 2.71(t, 2H); 5.17(m, 2H); 5.92(m, 1H);
7.18(m, 4H); 7.37(m, 1H)

^{13}C NMR: 32.6, 33.9, 114.8, 125.7, 127.5, 129.9, 138.1, 138.4,
143.0.

IR(neat, cm^{-1}): 3073.2, 2922.8, 1945.2, 1875.9, 1822.0, 1749.7,
911.8

UV/VIS: $\epsilon = 9700 \text{ L/mol cm}$ $\lambda_{\text{max}} = 247 \text{ nm}$

Elemental Analysis: Calculated for $C_{22}H_{24}$: C, 91.67%; H, 8.33%.

Found: C, 91.12%; H, 8.67%.

GC/MS: M^+ , 288.1858, $M(100)$, 205.1019%.

Synthesis of poly(5,6-diphenyl-1,5,9-decatriene) (48)

The monmer 47 was synthesized and dried as previously described. This reaction is analogous to the polymerization of 5-methyl-1,5,9-decatriene. Twenty milligrams of catalyst, $W(CHCMe_2R)(N-2,6-C_6H_3-iPr_2)[OCCH_3(CF_3)_2]_2$, where R= Phenyl, were added directly to the reaction flask that contained 2.0 gm of the monomer. The reaction was terminated via exposure to the atmosphere. The contents of the flask were dissolved in toluene and passed through a column of alumina, followed by freeze drying from chloroform. The clear polymer had the following spectral properties:

Yield: 94 %

1H NMR: 2.20(br, 2H); 2.74(br, 2H); 5.56(br, 1H); 7.15(br, 4H),
7.42(br, 1H).

^{13}C NMR: 26.2, 31.8, 32.4, 34.2, 114.8, 125.8, 126.6,
130.0(multiple signals), 138.1, 143.2, 143.4.

IR(neat, cm^{-1}): 3073.8, 2923.4, 1943.5, 1873.6, 1802.4, 1751.7,
910.4

UV/VIS: ϵ = 9700 L/mol cm λ_{max} = 247 nm

Elemental Analysis: Calculated for $C_{20}H_{20}$: C, 82.30%; H, 7.70%.

Found: C, 82.04%; H, 7.86%.

SEC (gm/mol): M_w = 12,400 PDI = 1.86

VPO (gm/mol): M_n = 6,360

TGA(onset): 373°C

DSC: T_g= 21°C

Metathesis Activity of Alpha Substituted Olefins

General Considerations

All reactions were allowed to proceed for 72 hrs with the motion of ethylene removal performed on an hourly basis for a minimum of ten hours per 24 hr period. Each reaction was allowed to react at room temperature of the first 24 hr period, after which, the flask was heated to 50°C with an oil bath. All reactions that showed a less than quantitative metathesis activity were repeated twice. The reagent recovered from the initial reactions were used for subsequent ones; therefore, if a reactant exhibited no reactivity, it was exposed to three separate aliquots of catalyst.

Following a non-productive reaction, the activity of the catalyst was tested by vacuum removal of all reagents followed by the addition of a known reactive diene, 1,9-decadiene.

Attempted metathesis of 3-methyl-1,4-pentadiene (49)

Compound 49 was purchased from Aldrich Chemical Co. as 99% pure and was dried as described above. In an argon filled dry box, 2.0 mL (16.4 mmol) of 3-methyl-1,4-pentadiene were added to a dried breakseal attached to a rotoflow™ valve. The valve was closed and the breakseal removed from the dry box and connected to the vacuum line. Once thoroughly degassed through freeze pump thaw cycles, the reactant was frozen in liquid nitrogen and the breakseal was sealed

off under full vacuum. The breakseal was connected to the reaction flask along with an analogously prepared breakseal containing 20 mg of dry catalyst $W(CHCMe_2R)(N-2,6-C_6H_3-iPr_2)[OCCH_3(CF_3)_2]_2$, where $R = \text{Phenyl}$. The reaction flask was then attached to the vacuum line, and flame dried under full vacuum. The catalyst breakseal was opened first, followed by the reagent containing breakseal. The liquid reagent was used to wash the catalyst into the reaction flask. Reaction conditions described above were followed. At the end of the 72 hour reaction period, all volatiles were transferred into a clean flask and analyzed.

Attempted metathesis of 3-methylhexene (50) with the tungsten catalyst (15)

Compound 50 was purchased from Fluka Chemicals as 99% pure and dried as already described. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $W(CHCMe_2R)(N-2,6-C_6H_3-iPr_2)[OCCH_3(CF_3)_2]_2$, where $R = \text{Phenyl}$, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

Metathesis of 3-Methylhexene (50) with the molybdenum catalyst (16)

Compound 50 was purchased from Fluka Chemicals as 99% pure and dried as already described. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $Mo(CHCMe_2R)(N-2,6-C_6H_3-iPr_2)[OCCH_3(CF_3)_2]_2$, where $R = \text{Phenyl}$, were used for this reaction. At

the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

The reaction medium contained a mixture of both isomers of 4,7-dimethyl-5-decene, with the following spectral properties:

Yield: 93%

^1H NMR: 0.85 (m, 12H); 1.37(m, 8H); 2.15(m, 2H); 5.25(dd, 2H)

^{13}C NMR: 14.1, 21.1, 36.2, 39.7, 134.4

Elemental Analysis: Calculated for $\text{C}_{12}\text{H}_{24}$: C, 85.71%; H, 14.29%

Found: C, 84.75%; H, 15.05%.

GC/MS: M^+ , 168.19; $\text{M}(100)$, 55.06

Metathesis of 3-methyl-1,5-hexadiene (52) with the tungsten catalyst (15)

Compound 52 was purchased from Fluka Chemicals as 99% pure and dried as described above. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{W}(\text{CHCMe}_2\text{R})(\text{N}-2,6-\text{C}_6\text{H}_3-i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

The reaction medium contained both isomers of 3,8-dimethyl-1,5,9-decatriene, with the following spectral properties:

Yield: 96%

^1H NMR: 0.97(d, 3H); 2.02(m, 3H); 4.95(m, 2H); 5.34(m, 1H);
5.78(m, 1H)

^{13}C NMR: 19.5, 34.4, 37.4, 39.9, 112.64, 128.89, 129.88, 144.38

Elemental Analysis: Calculated for $\text{C}_{12}\text{H}_{20}$: C, 87.80%; H, 12.20%.

Found: C, 87.05%; H, 12.45%.

GC/MS: M^+ , 164.19; $M(100)$, 70.00

Metathesis of vinylcyclohexane (58) with the tungsten catalyst (15)

Compound 58 was purchased from Aldrich Chemical Co. as 99% pure and dried as described above. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $W(CHCMe_2R)(N-2,6-C_6H_3-i-Pr_2)[OCCH_3(CF_3)_2]_2$, where $R = \text{Phenyl}$, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis. The collected clear liquid consisted mainly of starting material, but some dimer 1,2-dicyclohexylethene was produced.

Yield: 7.26 %(GC); 6.52 %(1H NMR)

1H NMR: 1.15(m, 5H); 1.63(br, 5H); 1.91(m, 1H); 5.31(dd, 1H)

^{13}C NMR: 26.1, 33.57, 33.87, 36.68, 40.90, 133.94, 134.30

GC/MS: M^+ , 192.188; $M(100)$, 96.094

Elemental Analysis: Calculated for $C_{14}H_{24}$: C, 87.50%; H, 12.50%.

Found: C, 87.01%; H, 12.57%.

Metathesis of vinylcyclohexane (58) with the molybdenum catalyst (16)

Compound 58 was purchased from Aldrich Chemical Co. as 99% pure and dried as described above. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $Mo(CHCMe_2R)(N-2,6-C_6H_3-i-Pr_2)[OCCH_3(CF_3)_2]_2$, where $R = \text{Phenyl}$, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum

transferred into a clean flask for analysis. The collected clear liquid consisted entirely of dimer, 1,2-dicyclohexylethene.

Yield: 96 %

^1H NMR: 1.15(m, 5H); 1.63(br, 5H); 1.91(m, 1H); 5.31(dd, 1H)

^{13}C NMR: 26.1, 33.57, 33.87, 36.68, 40.90, 133.94, 134.30

GC/MS: M^+ , 192.188; $\text{M}(100)$, 96.094

Elemental Analysis: Calculated for $\text{C}_{14}\text{H}_{24}$: C, 87.50%; H, 12.50%.

Found: C, 87.06%; H, 12.63%.

Metathesis of vinylcyclopentane (59) with the tungsten catalyst (15)

Compound 59 was purchased from Aldrich Chemical Co. as 99% pure and dried as described above. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty mg of $\text{W}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, was used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis. The collected clear liquid consisted mainly of starting material, but some dimer, 1,2-dicyclopentylethene, was produced.

Yield: 8.50 % (GC), 9.24 % (^1H NMR)

^1H NMR: 1.25 (m, 2H); 1.68(m, 6H); 2.34 (m, 1H); 5.38(m, 1H)

^{13}C NMR: 25.4, 33.8, 34.2, 38.1, 43.4, 133.1, 134.0

GC/MS: M^+ , 164.15; $\text{M}(100)$, 95.087

Elemental Analysis: Calculated for $\text{C}_{12}\text{H}_{20}$: C, 87.80%; H, 12.20%.

Found: C, 87.19%, H, 12.31%

Metathesis of vinylcyclopentane (59) with the molybdenum catalyst (16)

Compound 59 was purchased from Aldrich Chemical Co. as 99% pure and dried as described above. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N}-2,6-\text{C}_6\text{H}_3-i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis. The collected clear liquid consisted entirely of the dimer, 1,2-dicyclopentylethene.

Yield: 97 %

^1H NMR: 1.25 (m, 2H); 1.68(m, 6H); 2.34 (m, 1H); 5.38(m, 1H).

^{13}C NMR: 25.4, 33.8, 34.2, 38.1, 43.4, 133.1, 134.0.

GC/MS: M^+ , 164.15; $\text{M}(100)$, 95.087

Elemental Analysis: Caclulated for $\text{C}_{12}\text{H}_{20}$: C, 87.80%; H, 12.20%.

Found: C, 87.40%; H, 12.39%.

Synthesis of propenylcyclohexane (62)

Compound 62 was synthesized via the Wittig reaction.¹¹⁷ Fifty grams (135 mmol) of ethyltriphenylphosphonium bromide (Aldrich) were added to 200 mL of dry tetrahydrofuran under argon. This mixture was cooled to -78°C and 67.0 mL of a 2.0 molar solution of n-butyllithium was added via syringe, slowly with stirring. The mixture was allowed to warm the room temperature over several hours, during which all of the salt dissolved and the ylid was apparent by the red color of the solution. This solution was then cooled to -78°C and 14.0 mL (135 mmol) of cyclohexanone in 50

mL of THF was added slowly with stirring. This reaction solution was then warmed to room temperature, followed by refluxing for 12 hrs. The THF was then distilled out of the reaction flask and 200 mL of pentane added along with 200 mL of water. The pentane was decanted and the water extracted with another 100 mL of pentane. The combined pentane layers were washed with 50 mL portions of dilute HCl, water, NaHCO₃, and water. The pentane layer was then dried over MgSO₄ and filtered through alumina. The pentane was then removed by rotary evaporation, leaving a clear liquid.

Yield: 88 %

¹H NMR: 1.15(m, 5H); 1.71(m, 8H); 1.88(br, 0.4H); 2.32(m, 0.6H); 5.38(m 2H)

¹³C NMR: 18.00, 26.03, 33.81, 41.07, 122.24, 134.11, 138.35

Elemental Analysis: Calculated for C₉H₁₆: C, 87.10%; H, 12.90%

Found: C, 86.81%; H, 12.11%

GC/MS: M⁺, 124.1452; M(100), 81.0701

Metathesis of propenylcyclohexane (62) with the tungsten catalyst (15)

Compound 62 was synthesized and dried as already described. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of W(CHCMe₂R) N-2,6-C₆H₃-*i*-Pr₂)[OCCH₃(CF₃)₂]₂, where R= Phenyl, were used for this reaction. At the end of the 72 hour reaction period, all volatiles were vacuum transferred into a clean flask for analysis. The collected clear liquid consisted mostly of dimer 1,2-dicyclohexylethene and some unreacted starting material.

Yield: 82.63 %(GC)

^1H NMR: 1.15(m, 5H); 1.63(br, 5H); 1.91(m, 1H); 5.31(dd, 0.6H);
5.41(dd, 0.4H)

^{13}C NMR: 26.1, 33.57, 33.87, 36.68, 40.90, 133.94, 134.30

GC/MS: M^+ , 192.188; $\text{M}(100)$, 96.094

Elemental Analysis: Calculated for $\text{C}_{14}\text{H}_{24}$: C, 87.50%; H, 12.50%.

Found: C, 87.13%; H, 12.62%.

Synthesis of poly(3-methylbutenylenes) (67) with the molybdenum catalyst (16)

The monomer 3-methyl-1,5-hexadiene 52 was purchased from Fluka Chemicals as 99% pure and dried as described above. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where $\text{R} = \text{Phenyl}$, were used for this reaction. The reaction foamed vigorously initially, then the evolution of gas ceased. The reaction was taken into the dry box and sampled, followed by returning the flask to the vacuum line. After 48 hrs, the solution was visibly more viscous, and the evolution of gas, although slow, was observed. At this time the reaction was exposed to full static vacuum. Stirring the contents of the flask became impossible as its viscosity increased. The polymer was dissolved in toluene and passed through a column of alumina, followed by freeze drying from chloroform. The initial reaction sample was 3,8-dimethyl-1,3,5-decatriene. The resulting clear polymer had the following spectral properties:

Yield: 98%

^1H NMR: 0.97(d, 3H); 2.0(br, 3H); 5.29(br, 2H)

^{13}C NMR: 20.8, 32.3, 35.0, 36.6, 40.87, 127.15, 129.55, 130.12,
134.28, 136.63, 137.66

Elemental Analysis: Calculated for C_5H_8 : C, 88.24%; H, 11.76%.

Found: C, 87.64%; H, 12.06%.

SEC (gm/mol): $M_w = 11,720$ PDI= 1.93

VPO (gm/mol): $M_n = 5,800$

IR(neat, cm^{-1}): 2955.1, 1751.6, 1663.9, 1638.7, 1454.3,
966.8

DSC $T_g = -58^\circ\text{C}$

TGA (onset) 345°C

Synthesis of poly(*cis*-1,2-divinylcyclohexane) (69)

The monomer *cis*-1,2-divinylcyclohexane 68 was purchased from Flukla Chemicals as 99% pure and dried as already described. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. The reaction was allowed to continue until stirring via magnetic agitation became impossible. The resulting polymer was dissolved in toluene and passed through a column of alumina, followed by freeze drying from chloroform. The clear polymer had the following spectral properties:

Yield: 93 %

^1H NMR: 1.45(br, 6H); 2.23(br, 2H); 5.28(br, 0.2H); 5.41(br,
1.8H);

^{13}C NMR: 24.02, 25.25, 43.41, 43.86, 44.19, 113.84, 131.78,
132.02, 132.23, 141.83

SEC (gm/mol): Mw= 14,820 PDI= 1.90
 VPO (gm/mol): Mn= 7,960
 Elemental Analysis: Calculated for C₈H₁₂: C 88.89%; H, 11.11%.
 Found: C, 88.17%; H, 11.45%.
 IR(neat, cm⁻¹): 2919.5, 1718.2, 1447.5, 965.1
 TGA(onset): 266°C
 DSC: Tg= 22°C

Synthesis of *trans*-1,4-divinylcyclohexane (70)

The monomer *trans*-1,4-divinylcyclohexane 70 was synthesized following a modified procedure obtained from Dr. K. Schanze. Fifty grams (362 mmol) of cyclohexane-1,4-dimethanol was dissolved in 200 mL of dry pyridine; to this solution, 110 mL of benzoylchloride (950 mmol) was added at 0°C. This reaction was stirred for 2 hrs., then cooled to -30°C, at which time the crystals were collected by suction filtration. The crystals were dissolved in chloroform and washed with 100 mL portions of dilute HCl, water, NaHCO₃, and water again. The organic layer was dried over MgSO₄ and filtered, followed by removal of the solvent. The solid product was twice recrystallized from pure ethanol. The diester was 99.2 % *trans* by integration of ¹H NMR methine signal.

Yield: 37.5 grams, 48 %.

The *trans* diester was then saponafied back to the diol by refluxing in 250 mL of ethanol over 25 grams of KOH for three hours. The solution was filtered to remove salts. The ethanol was removed by rotoryevaporation and the solids dissolved in water. The unreacted ester was removed by extraction with pentane. The basic

aqueous layer was then acidified and again extracted with pentane. The water layer was then evaporated to dryness, and the solids washed with ethanol. The ethanol was evaporated leaving essentially pure *trans* (98.7 %) diol. Yield: 19.4 grams, 81%

The *trans* diol was then oxidized to the *trans* dialdehyde with pyridinium chlorochromate (PCC) in methylene chloride. Seven grams (48.6 mmol) of the dry diol was added to a mixture of 32.3 grams of PCC in 250 mL of CH₂Cl₂ and stirred for two hours. At this time, 250 mL of ether was added to the reaction and the liquid decanted. The solids were washed twice with 50 mL of ether and the ether layers combined. The liquid was passed through a pad of Florosil™ followed by removal by rotary evaporation. The unstable dialdehyde was not purified, but added directly to an awaiting THF solution of ylid. The ylid was prepared from methyltriphenylphosphonium bromide (Aldrich) and *n*-butyllithium as described above. The same work-up used for the synthesis of propenylcyclohexane was followed producing 3.5 grams of a clear liquid, *trans*-1,4-divinylcyclohexane.

Yield (overall for two steps): 61.6 %

¹H NMR: 1.17(m, 2H); 1.86(br, 3H); 4.93(m, 2H); 5.81(m, 1H)

¹³CNMR: 32.1, 41.4, 112.0, 112.6, 142.8, 144.4

Elemental Analysis: Calculated for C₁₀H₁₄: C, 89.55%; H, 10.45%.

Found: C, 89.05%; H, 10.72%.

GC/MS: M⁺, 136.1244; M(100), 107.1036

IR(neat, cm⁻¹): 2924.0, 1824.5, 1639.5, 1448.1, 993.6, 911.8

Synthesis of poly(*trans*-1,4-divinylcyclohexane) (71)

The monomer *trans*-1,4-divinylcyclohexane 70 was synthesized and dried as already described. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$, where R= Phenyl, were used for this reaction. The reaction was allowed to continue until stirring via magnetic agitation became impossible. The resulting polymer was dissolved in refluxing toluene and precipitated in cold methanol. The powdrous product had the following spectral properties:

Yield: 92 %

^1H NMR: 1.53(br, m, 4H); 2.15(br, m, 6H); 5.25(br, m, 0.8H);
5.6(br, 1.6H); 5.9(br, m, 0.4H)

^{13}C NMR: 29.5, 29.9, 32.1, 33.0, 40.5, 41.4, 112.1, 112.6, 133.8,
34.0, 144.4

SEC (gm/mol): $M_w = 1,500$ PDI= 1.40

Elemental Analysis: Calculated for $\text{C}_{42}\text{H}_{54}$ (pentamer): C, 90.57%;
H, 9.43%.

Found: C, 90.28%; H, 9.67%

TGA(onset): 278°C

DSC: $T_m = 118^\circ\text{C}$

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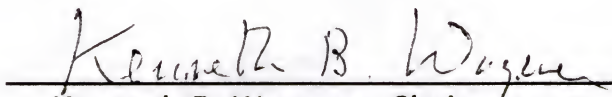
BIOGRAPHICAL SKETCH

The author was born in Jamaica, Queens, New York, on the 10th day of November in 1963, just twelve days prior to the assassination of President John F. Kennedy. At the age of 14, the author moved to the scenic mountains of North Carolina and upon graduation from high school, enrolled at North Carolina State University where he received a Bachelor of Science degree in biochemistry. While enrolled at N. C. State, the author got his first taste of research as a biological laboratory technician performing cancer research at the National Institute for Health in the Research Triangle Park.

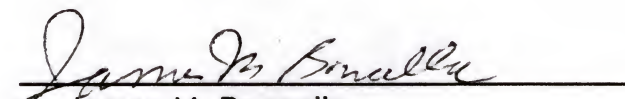
Upon graduation, the author was employed for three years as an assistant chemist at Southern Research Institute in Birmingham Alabama performing cancer research and later screening drugs for anti-HIV I activity. In preparation for graduate school as a chemist, the author attended the University of Alabama at Birmingham and earned a Bachelor of Science degree in chemistry. It was during this course of study that the author was enlightened about polymer chemistry by the late Dr. T. L. St. Pierre.

In 1988, the author relocated to Gainesville, Florida, to begin graduate studies in organic/polymer chemistry at the University of Florida under the direction of Dr. K. B. Wagener. The author was married on the fiftieth anniversary of Pearl Harbor Day, and completed his graduate studies on the same day of the next year, 1992. Graduation was official in May of 1993.


I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Kenneth B. Wagener, Chairman
Professor of Chemistry

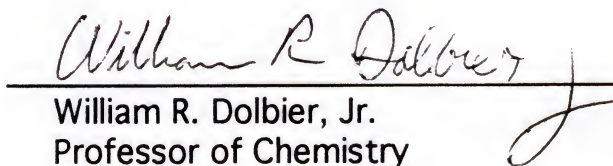
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James M. Boncella
Associate Professor of Chemistry

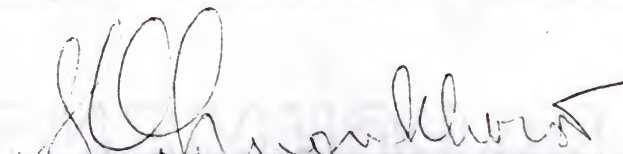
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John R. Reynolds
Associate Professor of Chemistry

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William R. Dolbier, Jr.
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Hendrik J. Monkhorst
Professor of Physics

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 1993

Dean, Graduate School